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Feasibility of Commercialized Water Treatment Techniques for Concentrated Waste Spills

TRW Environmental Engineering Div.
Redondo Beach, CA

Prepared for

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FEASIBILITY OF COMMERCIALIZED WATER TREATMENT TECHNIQUES FOR CONCENTRATED WASTE SPILLS

by

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Contract No. 68-03-2560

Project Officer

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The suitability and economics of using reverse osmosis, ultrafiltration, ion exchange, wet air oxidation, high purity oxygen activated sludge process, ultraviolet-ozone oxidation, and coagulation/precipitation for on-site treatment of concentrated wastes were evaluated. Published literature data and data obtained from process suppliers provided the basis for the evaluation.

When used alone, none of the processes considered would be economically applicable to on-site mobile unit treatment of the variety of concentrated wastes encountered, although reverse osmosis, ion exchange, and wet air oxidation meet many of the application requirements and hence require less pretreatment and/or post-treatment. The estimated capital costs for a unit suitable for trailer mounting vary from as low as \$35,000 for a 227,000 ℓ/day (60,000 gpd) ultrafiltration unit to as high as \$1.25 to \$1.5 million for a 54,000 ℓ/day (14,400 gpd) 2-trailer wet air oxidation unit. For short-term operation, the operating cost of the mobile unit is determined largely by non-process specific costs (for example, transportation, labor subsistence, analytical support, etc.), which vary from situation to situation.

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FOREWORD

The U.S. Environmental Protection Agency was created because of increasing public and government concern about the dangers of pollution to the health and welfare of the American people. Noxious air, foul water, and spoiled land are tragic testimonies to the deterioration of our natural environment. The complexity of that environment and the interplay of its components require a concentrated and integrated attack on the problem.

Research and development is that necessary first step in problem solution; it involves defining the problem, measuring its impact, and searching for solutions. The Municipal Environmental Research Laboratory develops new and improved technology and systems to prevent, treat, and manage wastewater and solid and hazardous waste pollutant discharges from municipal and community sources, to preserve and treat public drinking water supplies, and to minimize the adverse economic, social, health, and aesthetic effects of pollution. This publication is one of the products of that research and provides a most vital communications link between the researcher and the user community.

The suitability and economics of using reverse osmosis, ultrafiltration, ion exchange, wet air oxidation, high purity oxygen activated sludge process, ultraviolet-ozone oxidation, and coagulation/precipitation for on-site treatment of concentrated wastes were evaluated in this report.

Francis T. Mayo, Director
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SECTION 1

SUMMARY

Under a contract with EPA, an engineering evaluation has been made of the suitability of several commercially available water and wastewater treatment processes for use in mobile units for on-site treatment of highly contaminated waters encountered in hazardous materials spills situations. The processes evaluated are reverse osmosis, ultrafiltration, ion exchange, wet air oxidation, biological treatment, combined ozonation/ultraviolet radiation treatment, and coagulation/flocculation. Gravity separation, filtration, activated carbon adsorption, and incineration, which have been used or are under development for use in spill control situations, are also briefly reviewed.

The process evaluation is based on published literature and data obtained from process and equipment suppliers and assumes the use of a single trailer, 227,000 ℓ/day (60,000 gpd) hydraulic capacity, and the use of a process alone and not in combination with other processes in a treatment train. The evaluation criteria have included weight and size factors, capability for self-sustained operation, applicability to a diversity of waste types and contaminant concentrations, quick system startup and shutdown, minimum requirement for skilled labor, minimal intermedia pollution transfer potential, commercial availability or ease of fabrication of equipment, experience in mobile unit applications, and capital and operating costs.

REVERSE OSMOSIS (RO)

RO uses high pressures to force solvent (for example, water) through a membrane that is permeable to the solvent molecules but not to the solute molecules. Several types of membranes and membrane designs are available. RO is being used on a commercial scale to demineralize brackish waters and to treat a variety of industrial wastewaters (for example, food processing wastewaters, plating rinses, and cooling water blowdown). Numerous pilot plant studies have also been conducted or are under way to assess process suitability for the treatment of a range of industrial wastewaters, sea water, and biologically treated municipal sewage. RO is very effective in the removal of most dissolved organics, inorganic salts, heavy metals, and emulsified oils. Industrial wastewaters containing several thousand ppm of chemical oxygen demand (COD) and total dissolved solids (TDS) have been successfully treated with RO, as well as sea water that contains 3.5 percent TDS. One process developer has used RO in a 189,000 ℓ/day (50,000 gpd) unit for brackish water demineralization; the U.S. Army has a 54,500 ℓ/day mobile unit for field use to obtain potable water from brackish waters.

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RO meets many of the requirements for process use in a mobile spill control unit. RO units are compact, are commercially available, can be started and shut down relatively quickly, can be serviced conveniently, would produce only a small volume of residue (10 to 25 percent of the feed), would not require skilled field labor, and can be operated with the electric power produced on-site. The major shortcoming of the system is membrane susceptability to fouling or degradation caused by the presence of suspended solids or strong oxidizing chemicals in the wastewater or very low pH of the wastewater. Based on a preliminary design developed for a system using the "spiral wound" membrane design, the capital cost for a 227,000 ℓ/day (60,000 gpd) mobile RO system and support equipment has been estimated at $70,000. This cost does not include the trailer cost and costs for pretreatment equipment (for example, coagulation/filtration for suspended solids removal) that may be required. The operating cost per unit waste volume treated depends on the specific application (waste characteristics, site location, treatment chemicals required, etc.).

ULTRAFILTRATION (UF)

UF is a pressure-driven membrane separation process that operates at a lower pressure than RO and is suitable for applications involving larger molecules. Several types of membranes and membrane designs are offered commercially. To date, all reported full-scale uses of UF have been in industrial applications (for example, concentrating cheese whey, dye rinses, and emulsified oils). A number of pilot plant studies have also been conducted or are under way to treat other industrial wastewaters including wastes from Kraft pulp mills, laundries, and textile mills. In these applications, the process has proved effective in concentrating total solids, including color. Feed solids concentrations of as high as 46,300 ppm have been tested. When used in applications to high concentration wastewaters, the effluent may require additional treatment. Although UF has not been deployed in mobile units, process vendors have skid-mounted units that can be installed on a trailer; these units consist of one or two modules with hydraulic capacities in the 18,900 to 39,800 ℓ/day (5,000 to 10,000 gpd) range.

Sharing many characteristics of RO, UF meets nearly all key requirements for mobile unit application. The primary limitation of the system is inapplicability to wastes containing low molecular substances and for producing low concentration permeates from highly concentrated wastes. The capital cost for a 227,000 ℓ/day (60,000 gpd) spiral wound UF mobile unit is estimated at $35,000.

ION EXCHANGE

Ion exchange is a process whereby the toxic or undesirable ions in wastewater are replaced with relatively harmless ions. The exhausted resins are regenerated with acids, bases, or brine solutions. Exchange resins used in commercial applications are primarily made of synthetic organic materials. Recent advances in resins technology have involved development of "sorptive" resins that remove organics via adsorption rather than an ion exchange mechanism. Sorptive resins are regenerated with organic solvents or inorganic solutions of appropriate pH. Ion exchange resins are commonly employed in columnar beds through which the aqueous phase is passed in an upflow or downflow direction.

Ion exchange has been widely used in full-scale applications for water softening and boiler water treatment. Industrial wastewater treatment applications include treatment of electroplating wastewaters to recover chromium and water for reuse, mercury removal from chlor-alkali plant effluent, acid wastewater demineralization at an Army ammunition plant, color removal from pulp and paper mill effluent, recovery of ammonium nitrate from fertilizer production plant effluent, radioactive waste treatment at nuclear power plants, and recovery of phenols from concentrated industrial brines. Ion exchange can handle highly concentrated wastes; the process economics, however, may be unfavorable because of the requirement for frequent regeneration. Numerous pilot plant studies have been conducted or are currently under way to evaluate the applicability and economics of ion exchange for the treatment of various industrial wastewaters. Ion exchange process vendors have used a number of mobile ion exchange units for process treatability studies. A 276 ℓ/min (70 gpm) mobile unit has been used for tertiary treatment of domestic sewage.

Ion exchange meets nearly all the requirements for mobile unit spill control application. Ion exchange units are compact, are commercially available, are easily automated, can be started and shut down quickly, can handle a range of organic and inorganic concentrations (including highly acidic and alkaline wastes), can be serviced conveniently, would produce a small volume of residue that may be suitable for material recovery, and would not require skilled operating labor. Ion exchange is not an energy-intensive process, and the power required for pumping can be supplied by an on-board generator. Based on the data provided by one process supplier, a preliminary design has been prepared for a 227,000 ℓ/day (60,000 gpd) ion exchange system for use on a trailer flatbed. By loading the system with proper type(s) of resins (exchange resins and/or sorptive resins), the six-bed system can be used for demineralization of water low in inorganics, removal of both organic and inorganic substances, and removal of organics only. The total capital cost for the system is estimated at $140,000. The operating cost per unit volume of waste treated would vary with the speficic application and would be affected largely by waste characteristics that dictate the regeneration frequency. A total regeneration cost of $58 per cycle has been estimated for regeneration of one cation and one anion exchange column in the system with 5 percent solutions of HCl and NaOH. The corresponding cost for the regeneration of a sorptive resin column is estimated at $42, $400, and $1,150 for regeneration with 5 percent NaOH, methanol and acetone, respectively. No credit is taken for acetone or methanol, which may be potentially recovered via distillation of the spent regenerant.

WET AIR OXIDATION (WAO)

WAO involves aqueous phase oxidation of reduced inorganic and organic substances with air at relatively high temperatures and pressures. The process is especially suitable for the treatment of high strength or toxic organic wastes or wastes containing nonbiodegradable organics. Because oxidation takes place in an aqueous medium, air pollution problems are not generally associated with WAO. By proper selection of operating conditions (detention time, pressure, and temperature), any degree of oxidation (including complete destruction) of reduced substances can be achieved.

There are currently more than 150 WAO units in operation worldwide; about 90 percent of the units handle municipal sludges, whereas the rest process industrial wastes. Other reported commercial applications of WAO are for treatment of cyanide, photographic, acrylonitrile, and pulp mill wastes. On a pilot plant scale WAO has been applied to the treatment of explosives, pesticides, and plastic wastes. The process developer owns a 550 ℓ/day (155 gpd) WAO unit that it uses at the company headquarters for waste treatability studies; a 54,000 ℓ/day (14,000 gpd) mobile unit which will be mounted on two trailers is currently under design and should be available in 1981.

WAO does not meet all the requirements for use in a mobile spill control unit. The major system limitations are the small capacity of units suitable for trailer mounting; requirements for special design, material of construction, and skilled operating labor; and relatively high capital cost. The capital cost for the 54,000 ℓ/day (14,400 gpd) titanium-constructed unit is estimated at around $1.25 to $1.5 million. The operating costs are estimated at $15/hr for fuel and 2.5¢ per gallon of waste that is detoxified.

BIOLOGICAL TREATMENT

Biological oxidation involves the use of microorganisms to convert the dissolved and oxidizable organic matter to organic and inorganic end products and to agglomerating microbial flocs that can be removed by settling and/or filtration. Biological oxidation is most efficient and results in the production of stable end products when carried out aerobically, that is, in the presence of dissolved oxygen. The activated sludge process is one of the most widely used biological wastewater treatment processes. In the conventional design, air is provided to the wastewater in a reactor containing a high concentration of microbial flocs. The treated waste is then clarified prior to discharge; a portion of the settled sludge is recycled to the reactor, and the excess sludge is wasted. Use of high purity oxygen instead of air is one of the latest developments in activated sludge technology. Considerable saving in capital and operating cost is realized because of higher oxygen utilization efficiency that enables use of smaller equipment, reduces power consumption, and improves sludge settleability. High purity oxygen activated sludge, which is offered in this country under the trade names UNOX and OASES, has been evaluated in this study for use in mobile spill control units.

The high purity activated sludge process has been used in a number of large scale applications for the treatment of municipal and industrial wastewaters. Pilot plant treatability studies have also been carried out on a range of industrial wastewaters, including petrochemical, pulp mill, pharmaceutical, fruit canneries, brewery, and textile mill wastewaters. The most concentrated chemical wastes that have been treated without prior dilution have had COD values in the 1,000 to 3,000 range and have required long detention times (10 to 30 hours) to obtain high removal efficiencies. Union Carbide Corporation, the developer of the UNOX process, has seven mobile pilot plants having hydraulic capacities ranging from 27,000 to 217,000 ℓ/day (7,200 to 57,600 gpd). The company offers a total pilot plant program that includes the pilot plant equipment and necessary engineering services and supervision for plant operation.

The high purity activated sludge process does not meet some of the key requirements for use in a mobile spill control unit. System limitations include those inherent in biological processes (primarily, unsuitability for handling toxic or refractory wastes); long startup and stabilization period required; requirement for elaborate and lengthy bench-scale testing to determine treatability of complex wastes and optimum operating conditions; susceptibility to "shock" loads; unsuitability for treatment of wastewaters containing volatile hydrocarbons (because of explosion hazard), requirement for trained operating personnel; and very large reactor size required for handling concentrated wastes. It is estimated that the largest reactor size that can be accommodated on a single trailer is 47,300 ℓ (12,500 gal) that, at a detention time of 48 hours (which would be typically required for wastes containing 1,000-3,000 ppm of COD), would have a hydraulic capacity of only 23,650 ℓ/day (6,250 gpd). The purchase price for an existing UNOX mobile unit with a reactor volume of 6,050 ℓ (1,600 gal) is about $250,000.

COMBINED OZONATION AND ULTRAVIOLET RADIATION (O_3/UV)

O_3/UV is a newly-developed chemical oxidation process that has proved effective for the destruction of many organics, including refractory and toxic chemicals, organometallic complexes, and reduced inorganic substances. The oxidation takes place in a reactor where the waste is contacted with ozone and UV radiation simultaneously. The use of UV radiation enhances the oxidation power of ozone, thereby increasing oxidation rate and efficiency. Wastewater characteristics that influence process efficiency and hence system design are wastewater flow rate, nature and concentration of organics and suspended solids (which interfere with passage of UV light), and temperature.

Only a very limited number of full-scale units are reportedly in use today. These plants handle photographic and metal plating wastes from an Army ammunition plant and cyanide waste from a tool company. On a pilot plant scale, O_3/UV has been investigated for the treatment of "pink water" from ammunition plants, wastewater from field hospitals, PCB-containing wastewaters, and secondary effluent. No mobile O_3/UV unit is reportedly in operation today.

O_3/UV meets many of the requirements for applicability to the treatment of waste spills in a mobile unit. The major shortcoming of the system relates to the lack of extensive experience with the process and the limited amount of ozone that can be generated on-site. Because of ozone generation capacity limitations, highly concentrated wastes cannot be treated on-site without pretreatment. For spills containing 10 and 1,000 ppm TOC, the theoretical volumes of wastewater that can be treated in a mobile unit equipped with a 91 kg/day O_3 generator are 1,130,000 ℓ/day (300,000 gpd) and 11,300 ℓ/day (3,000 gpd), respectively. The capital cost for a 227,000 ℓ/day (60,000 gpd) mobile unit is estimated at $285,000. Fuel for the power generator is the major operating cost item. A 125 kw generator would consume about $6/hour of fuel.

CHEMICAL TREATMENT (PRECIPITATION/COAGULATION)

Addition of chemicals to wastewaters to precipitate dissolved substances and to coagulate colloidal particulates are widely used in the treatment of raw water supplies and industrial wastewaters. The treatment involves addition to and rapid mixing of the chemicals in the raw water, gentle mixing to promote floc growth, and settling and/or filtration for floc removal.

Precipitation results when the solubility of a compound is exceeded by addition of a "common ion". Many heavy metals can be precipitated as hydroxides or sulfides by addition of chemicals such as lime, sodium hydroxide, and sodium sulfide. The most widely used coagulants are aluminum and ferric salts. Coagulation is believed to result from the neutralization of the negative charge on the colloidal particles by the positively charged coagulant ions and their hydrolysis products and/or chemical reaction between the coagulant ions and the surface groups on the colloidal particles. Because of the many factors that affect coagulation efficiency (pH, nature, and concentration of organic and inorganic substances in water, coagulant dosage, temperature, etc.), no scientific method has yet been developed (despite extensive research) that would enable the determination of optimum coagulant dose based on some measurable raw water characteristics. In practice, the optimum coagulation conditions are determined by a "trial-and-error" approach using the "jar test".

At dosages that are commonly employed in the treatment of natural waters and dilute wastewaters (for example, municipal sewage), aluminum, ferric, and calcium salts have proved to be effective and economical for coagulation of particulates and precipitation of certain organic and inorganic substances. These coagulants, however, are not suitable for the treatment of concentrated wastes because of the very high chemical dosages required and the production of voluminous quantities of bulky sludges that must be separated, processed, and disposed of. In addition, these coagulants are ineffective in removing a broad spectrum of soluble organic and inorganic substances. From these standpoints, chemical coagulation alone is not suitable for use in a mobile spill control unit. The process, however, has been used in conjunction with filtration and carbon adsorption in the EPA's Mobile Physical/Chemical Treatment System.

MISCELLANEOUS PROCESSES

Miscellaneous processes that are reviewed are gravity separation, filtration, carbon adsorption, and thermal oxidation. The review of these processes is very brief and is intended primarily to make the study more "complete". These processes are commercially available and are widely used in municipal and industrial waste treatment applications. With the exception of thermal oxidation, these processes are also used in the EPA's Mobile Physical/Chemical Treatment System that has been employed in a number of spill control situations.

The EPA's Mobile Physical/Chemical Treatment System uses large rubber, collapsable, portable tanks, which are set up next to the trailer, for chemical coagulation and settling. The trailer houses three dual-media filters

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designed for a maximum filtration rate of 4.22 ℓ/sec (67 gpm) and three activated carbon columns containing 19.6 m^3 (700 ft^3) of carbon. The mobile unit has been in operation for six years, and considerable operating experience exists in actual applications to spill situations.

EPA has currently contracted out the work for design, construction, and demonstration of a mobile incineration system (Environmental Restoration Incinerator Complex, ERIC) for the destruction of residuals from hazardous material spill clean-up operations. The system, which will be mounted on three trailers, will use a rotary kiln incinerator equipped with afterburner, quench tower, and scrubber.

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SECTION 2

CONCLUSIONS

Based on the engineering evaluation described in this report, the following general conclusions can be offered on the suitability of reverse osmosis (RO), ultrafiltration (UF), ion exchange, wet air oxidation, biooxidation, ozonation/ultraviolet radiation (O_3/UV), and precipitation/coagulation processes for use in mobile units for on-site treatment and detoxification of spill-impacted waters.

- RO and ion exchange processes appear to meet many of the requirements for applicability of a process to the treatment of waste spills in a mobile unit. These processes offer low cost compact units, are commercially available, can be started and shut down relatively quickly, can be serviced conveniently, would not require skilled operating field labor, can be operated with electricity produced by on-board generators, can handle a spectrum of wastes including those containing high concentration of toxic substances and refractory organics, and produce a relatively small volume of waste residue requiring disposal. Both these processes have been used in mobile units for water and wastewater treatability studies.

- Wet air oxidation is particularly applicable to the destruction of refractory and toxic organics in concentrated wastes encountered in spill situations. The major limitations of the process are high capital cost, small capacity of trailer mounted units and the requirement for skilled operating personnel.

- While meeting many of the mobile unit application requirements, UF and O_3/UV suffer from the limitations of inapplicability to waste containing low molecular weight substances or highly concentrated large volume wastes, respectively. There is apparently no experience on the use of these processes in mobile units.

- High purity oxygen activated sludge process appears to be the preferred biooxidation system for possible use in mobile units. Biooxidation processes, in general, suffer from the following limitations that would make them unsuitable to be used alone in spill control situations: inapplicability to wastes containing high concentration of toxic substances and refractory organics; requirement for long detention time (and hence a large reactor size) for processing concentrated wastes; and considerable time required for process start-up and stabilization.

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- Aluminum, ferric, and calcium salts, at dosages that are commonly employed in the chemical treatment of raw waters and dilute wastewaters would not be effective in handling concentrated wastes. Use of much higher dosages that would be needed for concentrated wastes, results in the production of voluminous quantities of bulky sludges that are difficult to process for disposal.

- In general, very limited data are available on the performance of the candidate processes for use in mobile units in handling very concentrated wastes.

- Although some of the processes considered (for example, UF and O_3/UV) would be inapplicable to the treatment of certain spills (for example, wastes containing low molecular weight substances or large-volume concentrated wastes), they would be applicable to other types of spills (for example, dilute wastewaters or wastes containing large molecular weight substances).

- When used alone, none of the processes considered would be economically applicable to the treatment of the large variety of wastes encountered in spill situations. The applicability of these processes would be enhanced and the treatment costs would be reduced, however, if these processes are used in combination in a treatment train. The optimum process combination would vary with the spill type. The specific process combinations that would be applicable to the greater variety of spills need to be evaluated for possible deployment in mobile units.

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SECTION 3

INTRODUCTION

BACKGROUND AND STUDY OBJECTIVES

Even with the most comprehensive spill prevention programs, accidental spills of hazardous substances cannot be totally eliminated in an industrial society that handles and transports voluminous quantities of industrial chemicals and process wastes every day. Since spills generally occur at "unexpected" times and places, appropriate spill contaminant measures are seldom available or seldom can be delivered to the spill site on time to prevent spilled material from reaching nearby watercourses (ditches, ponds, streams, lakes, etc.). When a watercourse becomes contaminated, countermeasures including containment and treatment of the spill-impacted waters must be implemented as soon as practical to prevent further spread of pollution and to restore the watercourse to its pre-spill condition. A similar need for containment and on-site treatment of wastes and wastewaters has recently come to light with the discovery of sites where hazardous wastes have been improperly disposed of. The more publicized examples of such incidents have been the Pollution Abatement Services operation at Oswega, NY, the chemical disposal operation on the Albert Harris property at Ditmer, MO, and the former Hooker Chemical Corporation dump site at Love Canal at Niagara Falls, NY.

The need for emergency response capabilities for the treatment of leachate and wastes at hazardous waste dump sites and of spill-impacted waters at or near spill and dump sites has led the U.S. Environmental Protection Agency to carry out a number of programs aimed at the development of water and wastewater treatment technologies and associated hardware for such applications. These programs have led to the development and successful deployment of a Mobile Physical/Chemical Treatment System (employing chemical coagulation/flocculation, filtration, and activated carbon adsorption) and an on-going effort involving design, construction, and demonstration of a Mobile Environmental Restoration Incinerator Complex (ERIC).

The study described in this report, which has been carried out for the EPA, has had as its objective the engineering evaluation of a number of commercially available water and wastewater treatment processes for possible use in mobile units for on-site treatment and detoxification of spill-impacted waters containing high concentration of contaminants. The processes evaluated are as follows: reverse osmosis, ultrafiltration, ion exchange, wet air oxidation, biological treatment, combined ozonation/ultraviolet radiation, and coagulation/flocculation. To make the study more "complete", gravity separation, filtration, activated carbon adsorption, and incineration, which have

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been used in or are under development for spill control applications, have also been briefly reviewed. The engineering evaluation of the processes considered has been based on the information available in the published literature and the data obtained from process and equipment developers and vendors.

GENERAL REQUIREMENTS FOR USE OF A PROCESS IN A MOBILE UNIT

The characteristics listed below have been used as the general guidelines in the evaluation of the applicability of various processes to the treatment of concentrated waste spills. The mobile wastewater treatment system must:

(1) Be relatively light weight and small in size*. There are strict highway regulations that limit the size and weight of motor vehicles. The regulations vary from state to state. In California, vehicle dimensions are limited to the following: 12.2 m long, 2.4 m wide and 4.1 m high (40 ft by 8 ft by 13.5 ft). The weight limitation depends on the distance between the extreme axles and the number of axles on the vehicle. For a five-axle vehicle with a distance of 11 m (36 ft) between the first and last axles, the gross weight is limited to 29,900 Kg (66,000 lb). Although certain components of the system can be mounted on a separate vehicle, it would be preferred to have the entire unit (including auxiliary equipment) confined to a single unit to achieve greater operational flexibility and reduce cost and labor requirements.

(2) Be capable of self-sustained operation; that is, the unit should have an on-board power supply.

(3) Be capable of handling wastes having a range of physical and chemical properties as would be the case for a spectrum of chemicals that are encountered in different spill situations.

(4) Be capable of quick startup and shutdown and have minimum requirements for skilled labor.

(5) Be suitable for periodic operation and should not present special storage requirements.

(6) Present no, or minimum of, intermedia pollution transfer; any residue that is generated should be relatively small in volume and inoccuous.

(7) Be commercially available or be easily fabricated.

(8) Have reasonable capital and operating costs.

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*A treatment capacity of 227,000 ℓ/day (60,000 gpd) has been assumed in this study for the purpose of unit sizing and cost estimating.

ORGANIZATION OF THE REPORT

A separate chapter has been devoted in this report to each of the seven processes that have been analyzed in detail (Chapters 4 through 10). The discussion in each chapter includes a brief description of the process including operating principle, control parameters, flow diagrams, etc.; a survey of the most relevant commercial-scale and pilot plant applications to the treatment of municipal and industrial waters and wastewaters; a review of previous or existing mobile unit applications (if any); an evaluation of the process suitability for use in mobile units for on-site wastewater treatment (based on the criteria listed above); a preliminary conceptual design of a mobile unit; and an estimation of the capital and operating cost.

As noted previously, to make this study more complete, a brief review of gravity separation, filtration, carbon adsorption, and incineration (processes that have already been employed or are under design for employment in mobile unit spill control applications) has also been conducted. The results are presented in the last chapter of this report under the heading Miscellaneous Processes.

SECTION 4

REVERSE OSMOSIS

PROCESS DESCRIPTION

Process Principle

Reverse osmosis (RO) is a unit operation for producing waters low in dissolved solids from brackish waters and wastewaters. The process involves use of a semipermeable membrane that allows the passage of solvent (water) molecules but not the soluble molecules (both organic and inorganic compounds).

When a dilute and a concentrated solution are separated by a semipermeable membrane, there is a spontaneous transport of solvent from the dilute to the concentrated side of the membrane. The driving force for this phenomenon, referred to as osmosis, is the difference in the solvent vapor pressure on the two sides of the membrane. Equilibrium is reached between the two solutions at a certain pressure called the osmotic pressure, at which point the amount of solvent that passes in each direction through the semipermeable membrane is equal. The magnitude of the osmotic pressure is given by the Van't Hoff equation:

$$\pi = \eta RT \qquad (4.1)$$

where π = osmotic pressure, atm
η = solute concentration, moles/ℓ*
R = gas constant, 0.083 atm·ℓ/moles·°K
T = temperature, °K

By applying enough pressure to the concentrated solution to overcome the osmotic pressure, the flow of the solvent molecules can be reversed (that is, from the concentrated solution compartment to the dilute solution compartment). In water/wastewater treatment applications, this would result in the production of a product water (permeate) low in dissolved solids and a small volume of concentrated waste (reject) that can be sent to material recovery or further treatment/disposal.

The performance of a reverse osmosis system is determined by two parameters, the solvent (for example, water) flux and solute (for example, salt)

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*At high solute concentrations, use of solute activity in place of solute concentration would yield a more accurate value of osmotic pressure.

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permeability. The solvent flux, which determines the amount of water recovered, is given by the following equation:

$$J = K\ (\Delta P - \Delta\pi) \tag{4.2}$$

where J = solvent flux, $g/cm^2 \cdot sec$
K = water permeability coefficient, $g/cm^2 \cdot sec \cdot atm$ (value dependent on membrane characteristics and temperature)
$\Delta P = P_1 - P_2$; P_1 = applied pressure, atm
P_2 = pressure on downstream side of membrane, atm
$\Delta\pi = \pi_1 - \pi_2$; π_1 = osmotic pressure of the solution at the membrane interface, atm
π_2 = osmotic pressure of permeate, atm

In many cases, π_2 can be ignored and in tubular systems P_2 is atmospheric pressure and can also be ignored. The flux decreases with the increase in $\Delta\pi$, which in turn decreases with the lowering of solute concentration.

Even with the "best" systems, some solutes pass through the membrane. The amount of solute that passes through a unit area of membrane (that is, the solute flux) is independent of the applied pressure as indicated by the following equation:

$$F = \beta\ (C_H - C_L) \tag{4.3}$$

where F = solute flux, $g/cm^2 \cdot sec$
β = solute permeability coefficient, cm/sec
C_H = concentration of solute on high pressure side of membrane, g/cm^3
C_L = concentration of solute on low pressure side of membrane, g/cm^3

The solute flux affects the quality of the product water. Table 1 is a summary of the performance of RO for various chemical substances. In general, good removal can be expected for high molecular weight organics (for example, protein) and charged anions and cations. The degree of rejection (a) increases with the degree of ionization and the size of the charged ions and neutral molecules, (b) decreases with the hydrogen bonding tendency with the membrane, polarities of the molecules, and (c) is affected by molecular geometry and membrane characteristics (2,3).

Equations 4.2 and 4.3 show that while the solvent flux (J) increases with the increase in the applied pressure, the solute flux (F) is independent of the pressure. Thus, the higher the pressure the better is the quality and quantity of the water recovered. However, when too high a pressure is applied, the porous structure of the membrane is compressed, causing a decrease in flux. Optimum operating pressure for most membrane modules is around 2.5 to 4.2 MPa (350 to 600 psi).

Types of Membrane Modules

Membranes are usually fabricated in flat sheets or tubular forms and are assembled into modules. The most common materials used are cellulose acetate

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TABLE 1. PERCENT REJECTION OF SELECTED CATIONS, ANIONS, AND ORGANICS (1)*

Salts					
Cations†		Anions‡		Organics§	
Name	Percent rejection	Name	Percent rejection	Name	Percent rejection
Sodium	94-96	Chloride	94-95	Sucrose sugar	100
Calcium	96-98	Bicarbonate	95-96	Lactose sugar	100
Magnesium	96-98	Sulfate	89	Protein ($10{,}000^+$ M.W.)	100
Potassium	94-96	Nitrate	93-96	Glucose	99.9
Iron (Fe^{+2})	98-99	Fluoride	94-96	Phenol	---
Manganese (Mn^{+2})	98-99	Silicate	95-97	Acetic acid	---
Aluminum	99	Phosphate	99	Lactic acid	---
Ammonium	88-95	Bromide	94-96	Dyes (400 to 900 M.W.)	100
Copper (Cu^{+2})	96-99	Borate	35-70	Biochemical oxygen demand (BOD)	90-99
Nickel (Ni^{+2})	97-99	Chromate	90-98	Chemical oxygen demand (COD)	80-95
Strontium	96-99	Cyanide	90-95	Bacteria and virus	100
Hardness	96-98	Sulfite	98-99	Pyrogen	100
Cadmium	95-98	Thiosulfate	99		
Silver	94-96	Ferrocyanide	99		

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[*] Letter from I. Nusbaum, Fluid Systems Division, UOP, San Diego, CA, January 22, 1980.

[†] Aluminum, copper, nickel, and strontium may precipitate; in the presence of sulfate, calcium, borium, and strontium may be limiting; ammonium rejection is pH-dependent.

[‡] Fluoride, sulfate, sulfite, and silicate may precipitate; rejection of some anions (for example, borate and cyanide) is pH-dependent.

[§] Rejection of certain ionizable organics (for example, phenol, acetic acid, and lactic acid) is extremely pH-dependent; the data for phenol is characteristic of cellulose acetate membrane and not polyamide membrane; sucrose and lactose are not 100 percent rejected by conventional membranes and, operating at high concentrations, require elevated temperatures since viscosity would be a factor; COD and BOD rejections affected by the presence of low molecular weight organics; periodic disinfection of system would be required to maintain high rejections of bacteria, viruses, and pyrogens.

and other polymers such as polyamides. There are three basic module designs, tubular, hollow fiber, and spiral wound (see Figure 1). Each type of membrane module has its own advantages and limitations. The tubular module provides the largest flow channel and allows for turbulent fluid flow regime; thus, it is least susceptible to plugging caused by suspended solids and has the highest flux. However, because of its small area/volume ratio the total product recovered per module is small. The cost of a tubular module is approximately five times that for the other modules for an equivalent rate of water recovery (4), and the total space requirement is about three to five times that for the spiral wound system (5).

A hollow fiber membrane is constructed of polyamide polymers and cellulose triacetate by Dupont and Dow, respectively*. Polyamide membrane permits a wider operating pH range than cellulose acetate, which is commonly used for the construction of spiral wound and tubular membranes (see Table 2). Each fiber is about the size of a human hair. The flow channel and the flux are about an order of magnitude lower than the other configurations. This small flux, however, is compensated for by the large surface area/volume ratio, with the total product water per module being close to that obtainable with spiral wound modules. However, because of the small size of the channels (about 0.1 mm or 0.004 in.) and the laminar fluid flow regime within the channels, this module is most susceptible to plugging and may require extensive pretreatment to protect the membrane.

The spiral wound module consists of an envelope of flat sheet membranes rolled around a permeate collector tube (see Figure 1). This configuration provides for a higher flux (Table 1) and greater resistance to fouling than the hollow fiber modules; it is also less expensive and occupies less space than a tubular module.

PROCESS APPLICATIONS AND RELATED STUDIES

Commercial Scale Municipal/Industrial Applications

RO has played and continues to play an important role in desalination of brackish waters for municipal and industrial uses. In 1975, there were nearly 300 large (>95,000 ℓ/day) plants in operation around the world producing a total of 170 million liter per day (45 mgd) of purified water (6). Some data on these applications are summarized in Table 3.

RO has been used in full scale applications in food processing (7), in industrial wastewater treatment (8,9) (for example, plating rinses, cooling tower blowdown, pulp and paper spent liquor, acid mine drainage, petroleum stripping water), and in the treatment of agricultural wastewaters (10). There are more than 70 RO units in operation in the metal finishing and plating industry (4). There is little information on the performance of the RO units in these and other industrial wastewater treatment applications.

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*Letter from I. Nusbaum, Fluid Systems Division, UOP, San Diego, CA, January 22, 1980.

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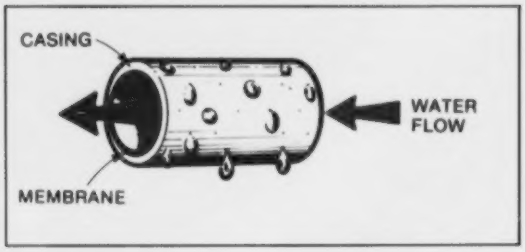
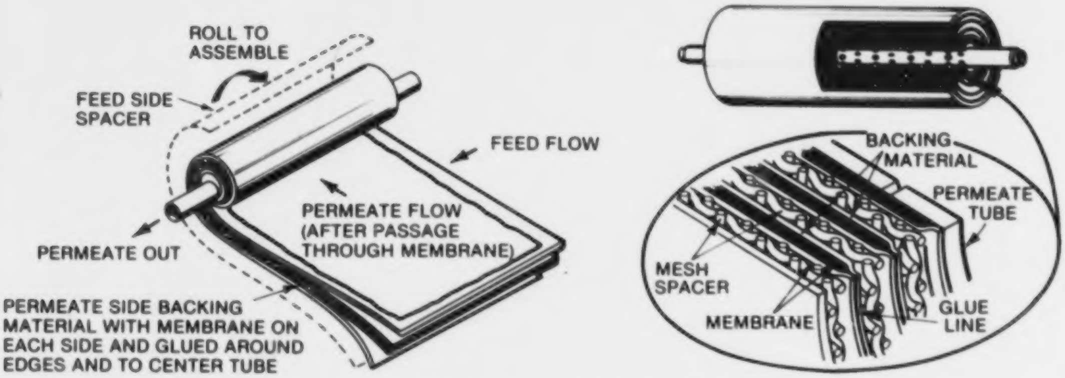
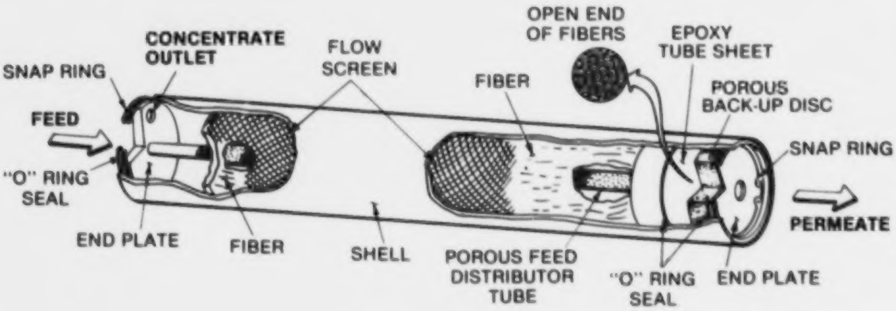

CASING
WATER FLOW
MEMBRANE

a. TUBULAR MEMBRANE


ROLL TO ASSEMBLE
FEED SIDE SPACER
FEED FLOW
PERMEATE FLOW (AFTER PASSAGE THROUGH MEMBRANE)
PERMEATE OUT
PERMEATE SIDE BACKING MATERIAL WITH MEMBRANE ON EACH SIDE AND GLUED AROUND EDGES AND TO CENTER TUBE
BACKING MATERIAL
PERMEATE TUBE
MESH SPACER
MEMBRANE
GLUE LINE

b. SPIRAL-WOUND MODULE


OPEN END OF FIBERS
EPOXY TUBE SHEET
CONCENTRATE OUTLET
FLOW SCREEN
SNAP RING
FIBER
POROUS BACK-UP DISC
FEED
SNAP RING
"O" RING SEAL
PERMEATE
END PLATE
FIBER
SHELL
POROUS FEED DISTRIBUTOR TUBE
"O" RING SEAL
END PLATE

c. HOLLOW-FIBER MODULE

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Figure 1. Membrane module configurations (4).

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TABLE 2. COMPARISON OF REVERSE OSMOSIS MODULE CONFIGURATIONS (1)*

	Spiral wrap	Tubular	Hollow fine fiber
Membrane surface area per volume, ft^2/ft^3	100 - 300	40 - 100	5,000 - 10,000
Product water flux, gpd/ft^2	8 - 25†	8 - 25	0.1 - 2
Typical module factors:			
Brine velocity, ft/sec	‡	1.5	0.04
Brine channel diameter, in	0.03§	0.5	0.004
Method of membrane replacement	As a membrane module assembly - on site	As tubes - on site	As entire pressure module - on site, module returned to factory
Membrane replacement labor	Low	High	Medium - requires equipment
High pressure limitation	Membrane compaction	Membrane compaction	Fiber collapse
Pressure drop, product water side	Medium	Low	High
Pressure drop, feed to brine exit	Medium	High	Low
Concentration polarization problem	Medium	High	High
Membrane cleaning - mechanical	No	Yes	No
- chemical	Yes - pH and solvent limited	Yes - pH and solvent limited	Yes - less restricted
Particulate in feed	Some filtration required	No problem	Filtration required
Permissible feed ranges, pH**	-	-	-
Permissible temperature, °F**	-	-	-

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*Letter from I. Nusbaum, Fluid Systems Division, UOP, San Diego, CA, January 22, 1980.

†Product flux varies with the net driving pressure and temperature; a flux of 10-25 gpd/ft^2 is typical at a pressure of about 400 psi.

‡It is difficult to define velocity in a spiral element since the space between membrane is filled with a polypropylene screen which acts as a spacer and turbulent promoter.

§Height of brine channel (not diameter).

**Permissible pH and temperature ranges dependent primarily on membrane type and not on module configuration; for example, polyamide hollow fine fiber is pH limited from 4 to 11, cellulose acetate from 3 to 7.5, thin film composite (TFC) spirals have been operated and cleaned at pH levels ranging from 1 to 12.

TABLE 3. DESIGNS AND OPERATING FEATURES FOR SOME COMMERCIAL RO PLANTS TREATING HIGH TDS WATERS

Application	Capacity 10^6 ℓ/d (gpd)	Module type	TDS, ppm Raw water	TDS, ppm Product water	Comment	Reference
Municipal (Florida)	1.9 (500,000)	Hollow fiber	8,000	<500	System designed for 50 percent water conversion, membrane is cleaned after every 870-1,700 hours of operation.	11
Computer manufacturer (Colorado)	0.19 (50,000)	Spiral wound	800	25	---	12
Boiler feedwater (Illinois)	1.8 (475,000)	---	550	50	Cost per 1,000 ℓ of product water is \$0.44 (\$1.68/1,000 gal)	13
Condensate makeup	0.22 (57,600)	Spiral wound	1,125	217	---	14

Pilot Laboratory Scale Studies

In addition to the actual process/wastewater treatment applications in the industry, a number of engineering/pilot-plant studies have been conducted or are currently in progress to assess the applicability of RO to the treatment of municipal and other industrial wastewaters and in connection with the development of improved membranes and RO systems. Some of the most pertinent of these studies are briefly described below.

A pilot-plant evaluation of the desalinization of sea water (TDS of 35,000 ppm) at the San Diego "Sea World" demonstrated that at an applied pressure of 7 mpa (1,000 psi) a product water with less than 300 ppm TDS can be obtained (15). Projected costs for this application ranged from $0.43/1,000 ℓ ($1.62/1,000 gal) for an 18.9 million ℓ/day (5 mpg) plant to $1.53/1,000 ℓ ($5.79/1,000 gal) for a 94,600 ℓ/day (24,000 gpd) plant.

The use of RO for the demineralization of acid mine drainage to produce low TDS waters suitable for domestic and industrial purposes has been demonstrated by Fluid Systems (previously Gulf) (16,17) (see Table 4).

TABLE 4. USE OF RO FOR THE DEMINERALIZATION OF ACID MINE DRAINAGE (17)*

Parameters/constituents	Value	
	Raw water	Treated water
pH	3.6	3.9
Fe (total)	100	2
SO_4	1,580	21
Ca	185	1.5
Al	27	1

*Except for pH, all values are in mg/l.

Laboratory and pilot studies on the removal of nutrients from raw and secondary treated wastewaters have indicated the following removal efficiencies (18): phosphorus - 100 percent, ammonia - 85 percent, and nitrate and nitrite - 56 percent*. A spiral wound module tested at the Los Angeles County Sanitation District demonstrated the feasibility of using RO for tertiary treatment of municipal wastewaters. In this demonstration effort, it was found that membrane deposits contained large amounts of polyhydroxy aromatic compounds and substances containing carboxylic acid groups. The flux could be restored by periodic treatment with detergent and relaxation of the applied pressure (19).

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*By proper pH adjustment, ammonia removal of better than 95 percent can readily be obtained; new thin film composite (TFC) membranes attain NO_3 removal of 98 percent (letter from I. Nusbaum, Fluid Systems Division, UOP, San Diego, CA, January 22, 1980).

The feasibility of the application of RO for concentrating soluble oil coolants in a wastewater was demonstrated in a 2,650 ℓ/day (700 gpd) pilot study (20). The data on the system performance after 3,000 hours of on-line operation are summarized in Table 5. Since RO approaches the absolute filter, the rejection of oil and suspended material is near perfect but fouling problems would essentially negate this application for anything except possibly tubular system*.

TABLE 5. USE OF RO FOR THE TREATMENT OF AN OILY WASTEWATER (20)

Constituents	Concentrations, ppm		Percent removal
	Feed	Treated water	
TDS	1,404	39	97.2
TOC	2,000	50	97.5
COD	6,900	150	97.8
BOD_5	9,000	82	90.9
Phenol	1.32	0.72	45.5
Oil	2,400	6	99.7

Very few studies appear to have been conducted to evaluate the effectiveness of RO for the removal of specific organic compounds. In a laboratory study, RO was shown to be capable of removing better than 99 percent of 15 major pesticides (7 chlorinated hydrocarbons, 4 organophosphorus, and 4 other types of pesticides) for wastewaters containing pesticide concentrations ranging from 40 ppb to 1.5 ppm (21). Part of the removal was attributed to the adsorption of pesticides on the membrane.

In another laboratory study, an average rejection of 12 to 80 percent was found for 13 low molecular weight polar organic compounds, including methanol, ethanol, isopropanol, acetic acid, formaldehyde, acetone, ethyl ether, urea, glycerol, phenol, hydroquinone, aniline, and methyl acetate (22). Synthetic solutions having a TOC of 1,000 ppm were used as feed in these experiments.

The reported data on the effectiveness of RO for the removal of phenols are inconsistent. A 45 percent removal of phenol was observed in one study

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*Letter from I. Nusbaum, Fluid Systems Division, UOP, San Diego, CA, January 22, 1980.

(20) whereas a "negative" removal was reported in another (6). Phenol rejection is a function of pH and membrane type.

Mobile Unit Applications

Use of RO in mobile systems for the treatment of brackish waters has been demonstrated in a number of applications. Some of these applications are briefly discussed below.

In 1969, Envirogenics (El Monte, CA) used a 189,000 ℓ/day (50,000 gpd) trailer-mounted "plate-and-frame"* RO unit for the treatment of brackish waters (23). In 1978 the company built another trailer-mounted RO unit using the spiral wound design. The unit could be operated on either a 50 or 60 cycle external power source or from a diesel generator (24). Recently, the U.S. Army has constructed a 54,500 ℓ/day (14,400 gpd) mobile unit to provide potable water in the field from any fresh, brackish, or sea water source (25).

The U.S. Army has also tested a lightweight, hand-operated tubular RO unit with the following characteristics (26): size - 0.0085 m^3 (0.3 ft^3), dry weight - 4.7 kg (10.3 lb), wet weight - 5.7 kg (12.6 lb), design capacity - 500 ℓ/day (135 gpd), and design performance - 70 percent product water recovery and 90 percent salt rejection.

USE OF RO IN MOBILE UNITS FOR TREATMENT OF WASTE SPILLS

This section evaluates the feasibility of using RO in a mobile unit to treat concentrated waste spills.

Pertinent Features of RO for Use in Mobile Units

In general, nearly all the requirements discussed in Section 3 for applicability of a systems to the treatment of waste spills in a mobile unit would be met by RO. RO units are compact, are commercially available, can be started and shut down relatively quickly, can be serviced conveniently, would generally produce only a small volume of residue, would not require skilled field labor for operation, and can be operated with the electric power produced on-site by a diesel generator. The major shortcomings of the RO unit relate to possible membrane fouling by suspended solids; membrane degradation due to very low or high pH levels (depending on membrane type); presence of strong oxidizing chemicals, high levels of phenol and phenolic substances, and organic solvents; and generation of a reject requiring ultimate disposal.

As discussed earlier in this section, RO is a commercial process, is offered by a number of manufacturers†, and has been used in mobile water treat-

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[*] The "plate-and-frame" units represent the early stage of RO development and have been abandoned in favor of newer membrane designs (spiral wound, etc.).

[†] Partial list of RO manufacturers and suppliers: Aqua Media, Sunnyvale, CA; Dow, Walnut Creek, CA; DuPont, Wilmington, DE; Envirogenics, El Monte, CA; Hydronautics, Santa Barbara, CA; Permutit, Paramus, NJ; Polymetrics, San Jose, CA; UOP, San Diego, CA.

ment applications. The unit is fairly compact; a 5,680 ℓ/day (1,500 gpd) product water capacity unit using the spiral wound module design would weight about 36 kg (8 lb) and would be approximately 10 cm (4 in) in diameter and 100 cm (40 in) in length. The startup and shutdown of RO consist primarily of turning on-and-off of the high pressure pump and adjusting the pressure and flow control valves. RO modules are connected in series or in parallel with provisions for flow by-pass so that a single module can be by-passed for maintenance service. Operation of RO units does not require highly skilled labor; the operating effort would be limited to turning valves, reading gauges, and collecting samples for chemical analysis. In mobile unit applications, the system would be equipped with on-line monitors for continuous measurement of pH, temperature, pressure, etc. Ordinarily no more than 6 to 12 operator-hours would be required for a 24-hour operation of an RO unit. For safety reasons, however, operation of a mobile unit in the field may require a minimum of 2 persons. The power for the operation of an RO unit can be provided by a diesel electric generator that can be housed in the same mobile unit. Approximately 2.6 kw of electricity would be required to produce 1,000 ℓ of product water (10 kw/1,000 gal).

As with any wastewater treatment system, RO produces a residue (reject) that requires disposal. The volume of this reject (waste concentrate) is usually about 10 to 25 percent of the volume of feed water. In field applications, the reject may be collected in drums and subsequently transported to hazardous waste management facilities or municipal sewage treatment plants for further treatment/disposal.

As with all membrane processes, RO units are susceptible to membrane fouling and deterioration. Waste spills would generally contain suspended solids/debris and may also contain chemicals that can attack the membrane materials. Suspended solids in the waste can be removed by pretreatment using mixed-media filters followed by cartridge filtration (for example, through 10-25 μ filters). The growth of slimy biomass on the membrane surface or the presence of organic macromolecules in the waste may also foul up the membrane. This organic fouling can be minimized by pre-chlorination, addition of biocides, and/or pretreatment with carbon adsorption. Membrane fouling can also result from precipitate (scale) formation as the waste becomes concentrated. The precipitates that would be most commonly encountered are those of calcium salts (primarily carbonate and sulfate). Scale formation can be minimized by adjusting the pH and/or the use of "scale inhibitors" such as polyphosphates.

Choice of Membrane Configuration

There are three basic membrane module configurations (designs). Although the general performance (with respect to salt rejection) is similar for the three membrane designs, there are certain design features and membrane properties that make one design superior to others under certain conditions (for example, pH or presence of suspended solids) and inferior under other conditions (see Table 2 for comparison of RO module configurations).

In general, the hollow fiber modules with polyamide membranes can be operated over a wider pH range than the tubular or the spiral wound modules that commonly use cellulose acetate membranes. At relatively low pH levels,

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the cellulose acetate is susceptible to degradation via hydrolysis. Wastewater having too high or too low pH values would require pH adjustment by addition of acid or base prior to treatment in RO units employing spiral wound or tubular module designs.

Hollow fiber modules with polyamide membranes are more susceptible to chlorine attack than the spiral wound and the tubular modules. A chlorine concentration of as low as 0.1 ppm can cause degradation of the hollow fiber membranes. Spiral wound and tubular membranes can tolerate up to 1 ppm of free chlorine (28).

Having much narrower passages for wastewater flow, the hollow fiber configuration is considerably more susceptible to fouling and hence, less desirable for waste spill treatment application than tubular or spiral wound designs. Membrane fouling can result from the presence of suspended solids in the waste. The solids may be initially present in the wastewater or may be produced during treatment as a result of chemical precipitation (for example, of calcium sulfate or carbonate) brought about as the waste becomes more concentrated. Although suspended solids can be removed by prior filtration and the precipitate formation can be minimized by use of chemical additives, the requirement for filtration or chemical addition would be less for the tubular and spiral wound designs than for the hollow fiber design.

Because of its relatively smaller membrane surface area to module volume ratio, a tubular module would occupy a larger space (approximately 4 times as much) than the hollow fiber or the spiral wound modules for the same water throughput. This would constitute a disadvantage for the tubular module for use in a mobile unit that would require a small equipment volume. Another disadvantage of the tubular module is its relatively high cost. For the same throughput capacity, the capital cost for a tubular design is about five times as much as that for a spiral wound design.

Table 6 summarizes the relative advantages and disadvantages of the three modules for use in spills treatment mobile units. Even though the tubular design would be less susceptible to fouling, it would probably be less suitable for use in mobile units because of its larger size (and higher cost) than the spiral wound or the hollow fiber designs. The spiral wound appears to be more desirable than the hollow fiber design primarily because of its lower susceptibility to fouling that significantly reduces the pretreatment requirements. Accordingly, in the following section, only the spiral wound design has been evaluated and costed for use in mobile treatment units.

Engineering Evaluation and Cost Estimates

Based on data obtained from one RO manufacturer*, a preliminary design has been developed for a 227,000 ℓ/day (60,000 gpd) spiral wound RO unit for use on a trailer flatbed. Figure 2 presents the flow diagram for the system

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*Telephone communication with Frank Trabert, Envirogenics Company, El Monte, CA, January 19, 1979.

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TABLE 6. COMPARISON OF THE THREE RO MODULES FOR USE IN SPILLS TREATMENT MOBILE UNITS

Parameter	Hollow fiber	Tubular	Spiral wound
Broad pH range of applicability*	Yes	No	No
Relative susceptibility to fouling by suspended solids	High	Low	Medium
Relative unit size (4)	1	4	1
Relative cost (5)	1	5	1

*As noted previously, pH range of applicability is dependent on membrane type and not on module design; spiral wound TFC would have the broadest pH range of applicability.

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based on design recommendations by an RO manufacturer*. The system, which consists of ten pressure vessels arranged in four stages, can be mounted on two heavy skids with five vessels on each skid. Each vessel contains six modules. Excluding the equipment for pretreatment, the system would have dimensions of 8 m long, 1 m wide, and 2.6 m high (24 ft x 3 ft x 8 ft), would weigh about 2,720 kg (6,000 lb) and would occupy 20.8 m^3 (576 ft^3) of space. The water recovery is estimated at 90 percent. Other components of the system (not all of which are shown in the figure) include a high pressure pump, pretreatment equipment (cartridge filters, carbon adsorption, chemical feed system), valves and piping, pressure valves, instrument panel, and the power supply source. Power can be supplied to the unit using a diesel electric generator. The generator, a 30 kw unit, would have the approximate dimensions of 2 m (l) x 0.8 m (w) x 1.1 m (h), 6 ft x 2 ft x 3.5 ft, would weight approximately 900 kg (2,000 lb), and would occupy a volume of 1.8 m^3 (42 ft^3). A storage tank having a volume of about 1.9 m^3 (500 gal) would supply the fuel to the unit.

The major logistics support required in field applications relate to possible requirements for membrane replacement and sufficient supply of treatment chemicals (acid, base, scale inhibitors, etc.). Under normal operation, it is unlikely that membrane replacement would be required during short-term field operation. In application to brackish water treatment, a membrane life of 2 to 3 years has been reported for continuous operation. Lower membrane life would be expected in application to concentrated waste spills. Assuming a requirement for replacement of 50 percent of the modules during a field application, the volume of the spare modules which may have to be carried onboard is about 0.24 m^3 (8.7 ft^3).

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*Telephone communication with Frank Trabert, Envirogenics Company, El Monte, CA, January 19, 1979.

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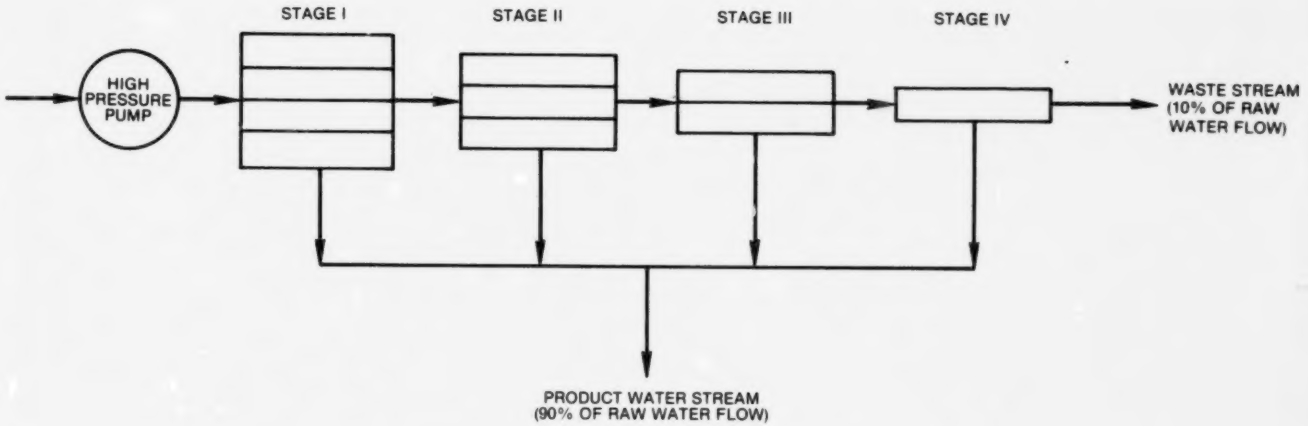
STAGE I
STAGE II
STAGE III
STAGE IV
HIGH PRESSURE PUMP
WASTE STREAM (10% OF RAW WATER FLOW)
PRODUCT WATER STREAM (90% OF RAW WATER FLOW)

Figure 2. 4-stage module arrangement for a 227,000 ℓ/day (60,000 gal/day) mobile RO treatment system.

Chemical requirements are determined by the characteristics of a specific waste spill. The quantity of the chemicals which may have to be carried onboard for short-term field operation would be relatively small[*]. For extended field operation, the mobile unit may have to be resupplied with chemicals on an as necessary basis.

The estimated total capital costs for the RO unit[†] and the diesel electric generator[‡] are $60,000 and $10,000, respectively. The cost for the RO unit does not include costs for pretreatment equipment. It does, however, include costs for RO modules, piping, valves, high pressure pump, chemical storage tank, chemical feed pumps, and the instrumentation panel. The cost also covers the engineering and installation fee.

The operating cost for the mobile RO unit per unit volume of waste treated should vary depending on the specific application (for example, waste characteristics, waste volume chemicals requirement, location of the spill, etc.). Assuming that in most field applications the mobile unit will have to be powered by a diesel electric generator, the fuel for the generator would constitute one of the major items of operating cost. A 30 kw diesel generator would consume about 11 ℓ/hr (3 gal/hr) of fuel (about $2/hr)[‡].

REFERENCES

1. Bureau of Reclamation and Office of Saline Water, Desalting Handbook for Planners, May 1972.

2. Duvel, W.A., Jr. & T. Helfgott. Removal of Wastewater Organics by Reverse Osmosis, Journal of Water Pollution Control Federation, Vol. 47, No. 1, p. 57, Jan. 1975.

3. Weber, W.J., Jr. Physicochemical Processes for Water Quality Control, Wiley-Interscience, New York, 1972.

4. McNulty, K.J., D.G. Grant, et al. Treatment of Metal Finishing Wastes by Reverse Osmosis, AIChE Symposium Series, No. 166, Vol. 73; Water-1976: I. Physical, Chemical Wastewater Treatment; p. 176, 1977.

5. Mason, D.G. Engineering Evaluation of Reverse Osmosis and Ion Exchange: Demineralization for use in a Self-Sustained, Air-Transportable Wastewater Renovation Unit. Interim Technical Report, AFSC Report AD-840 198/6ST, 1968.

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[*] Assuming that a dose of 100 ppm HCl would be used for pH adjustment, the acid requirement would only be 100 g/1,000 ℓ (0.8 lb/1,000 gal). Ordinarily, much lower quantities of other chemicals (for example, scale inhibitors) would be required because of the much lower dosages used.

[†] Telephone communication with Frank Trabert, Envirogenics Company, El Monte, CA, January 19, 1979.

[‡] Telephone communication with L. Anderson, Anderson-Belviar Company, Long Beach, CA, January 31, 1979.

6. Arthur D. Little. Physical, Chemical, and Biological Treatment Techniques for Industrial Wastes. PB-275-287, EPA Office of Solid Waste Management Programs, 1976.

7. Water Purification Associates. Innovative Technologies for Water Pollution Abatement, PB-247-390, 1976.

8. Witmer, F.E. Reusing Wastewater by Desalination, Environmental Science and Technology, Vol. 7, No. 314, 1973.

9. Kremen, S.S. Reverse Osmosis Makes High Quality Water Now, Environmental Science and Technology, Vol. 9, No. 314, 1975.

10. Blanton, M. California's Water Reclamation and Desalination Projects, Water and Sewage Works, Vol. 124, No. 6, 1977, p. 60.

11. McIntosh, A.L. Florida Reverse Osmosis Plant Turns Out Potable Water, Water and Sewage Works, Vol. 124, No. 12, 1977, p. 30.

12. Cruver, J.E. Reverse Osmosis - Where It Stands Today, Water and Sewage Works, Vol. 120, No. 10, 1973, p. 74.

13. Loeb, M.B. and R. Schuler. RO Units Cut Cost of Feedwater Treatment, Power Engineering, December 1978, p. 57.

14. Wadlington, M. Chemical Regenerant Savings Can Pay for a Reverse Osmosis Unit, Industrial Water Engineering, Vol. 13, No. 3, 1976, p. 17.

15. Cruver, J.E. and J.H. Sleigh. Reverse Osmosis - The Emerging Answer to Seawater Desalination, Industrial Water Engineering, Vol. 13, No. 3, 1976, p. 8.

16. Kremer, S.S., A.B. Reidinger, et al. Reverse Osmosis Field Testing on Acid Mine Waters at Norton, West Virginia, Research and Development Progress Report No. 586, U.S. Department of Interior, 1970.

17. Gulf Environmental Systems Company, Acid Mine Waste Treatment Using Reverse Osmosis, Water Pollution Control Research Series 140/ODYG, August 1971.

18. Lim, H.S. and H.K. Johnston. Reverse Osmosis as an Advanced Treatment Process, Journal of Water Pollution Control Federation, Vol. 48, No. 7, p. 1804, July 1976.

19. Cruver, J.E. and I. Nusbaum. Application of Reverse Osmosis to Wastewater Treatment, Journal of Water Pollution Control Federation, Vol. 46, No. 2, Feb. 1974, p. 301.

20. Markind, J., J.S. Neri, et al. Use of Reverse Osmosis for Concentrating Waste-Soluble 0.1 Coolants, Water - 1975, AIChE Symposium Series, No. 151, Vol. 71, p. 70, 1976.

21. Chian, E.S.K., W.N. Bruce, et al. Removal of Pesticides by Reverse Osmosis, Environmental Science & Technology, Vol. 9, No. 1, p. 52, Jan. 1975.

22. Fang, H.H.P. and E.S.K. Chian. Reverse Osmosis Separation of Polar Organic Compounds in Aqueous Solution, Environmental Science and Technology, Vol. 10, No. 4, p. 364, April 1976.

23. Watson, Z.K. Design and Fabrication of a 50,000 GPD Portable Reverse Osmosis Pilot Plant, Research and Development Progress Report 431, Department of Interior, 1969.

24. Envirogenics Systems Company, Newsletter, Vol. 2, No. 1, May 1978.

25. Schmitt, R.P. and R.P. Carnahan. U.S. Army Mobility Equipment Research and Development Command, Environmental Pollution Abatement Program, Industrial Water Engineering, Vol. 13, No. 1, p. 25, 1976.

26. Williams, R.H., D.R. Fort, et al. Lightweight, Hand-Operated Brackish Water Purifier, AD-782119, 1974.

SECTION 5

ULTRAFILTRATION

PROCESS DESCRIPTION

Process Principle

Ultrafiltration (UF) is a pressure-driven separation process that employs semipermeable membranes operating under dynamic flow conditions. The process is especially suitable for concentrating dilute products or recovering water or certain chemicals from waste streams. Figure 3 compares the particle separation capability of UF with those of reverse osmosis, microporous filters, and conventional filters. At the small-molecule/low flux end of the scale lies the commercial cellulose acetate reverse osmosis membranes with the capability of retaining hydrated sodium and chloride ions. Next on the scale is UF membranes with pores that cover a size range of about 10^{-3} to 10^{-2} microns (10-100Å) with filtration fluxes of about 0.5 to 10 gallons/sq ft/day/psi of pressure-driving force. Compared to the reverse osmosis process that operates at a pressure of 2.6 to 4.2 mpa (350 to 600 psi), UF operates at much lower pressure, usually around 0.18 to 1.1 mpa (25 to 1,250 psi). UF can operate at such low pressures because unlike RO, which is affected by the osmotic pressure of the solutes, the osmotic pressure of the materials retained by UF membranes is so low that it does not significantly influence the solvent flux, and RO membranes are nonporous diffusion barriers, while UF membranes are microporous structures.

In actual UF operation, the degree of separation or the amount of water recovered (flux) depends on the physical properties of the membranes such as porosity and thickness, and system variables such as pressure, temperature, feed velocity, and waste composition. Semipermeable membranes used in the UF process are porous structures made of organic polymers such as cellulose acetate or inorganic chemicals such as zirconium oxide. The membranes have an extremely thin (0.1 to 1 μ) with an effective pore size of about 0.002 μ (20 Å) or larger (2). Solute molecules or particles larger than the membrane pore size would be retained by the membrane while the smaller molecules or particles would penetrate the membrane with the solvent (water) and are collected as permeates. In general, dissolved salts and small organic molecules are not retained by UF membranes. The lower and upper molecular weight cutoff limits are around 500 and 500,000, respectively (3). The solute molecules or particles to be separated by the UF process should be at least one to two orders of magnitude larger than the solvent molecules (2). With the advancement in membrane technology, the membrane porosity can be "custom made" for specific molecular size separations.

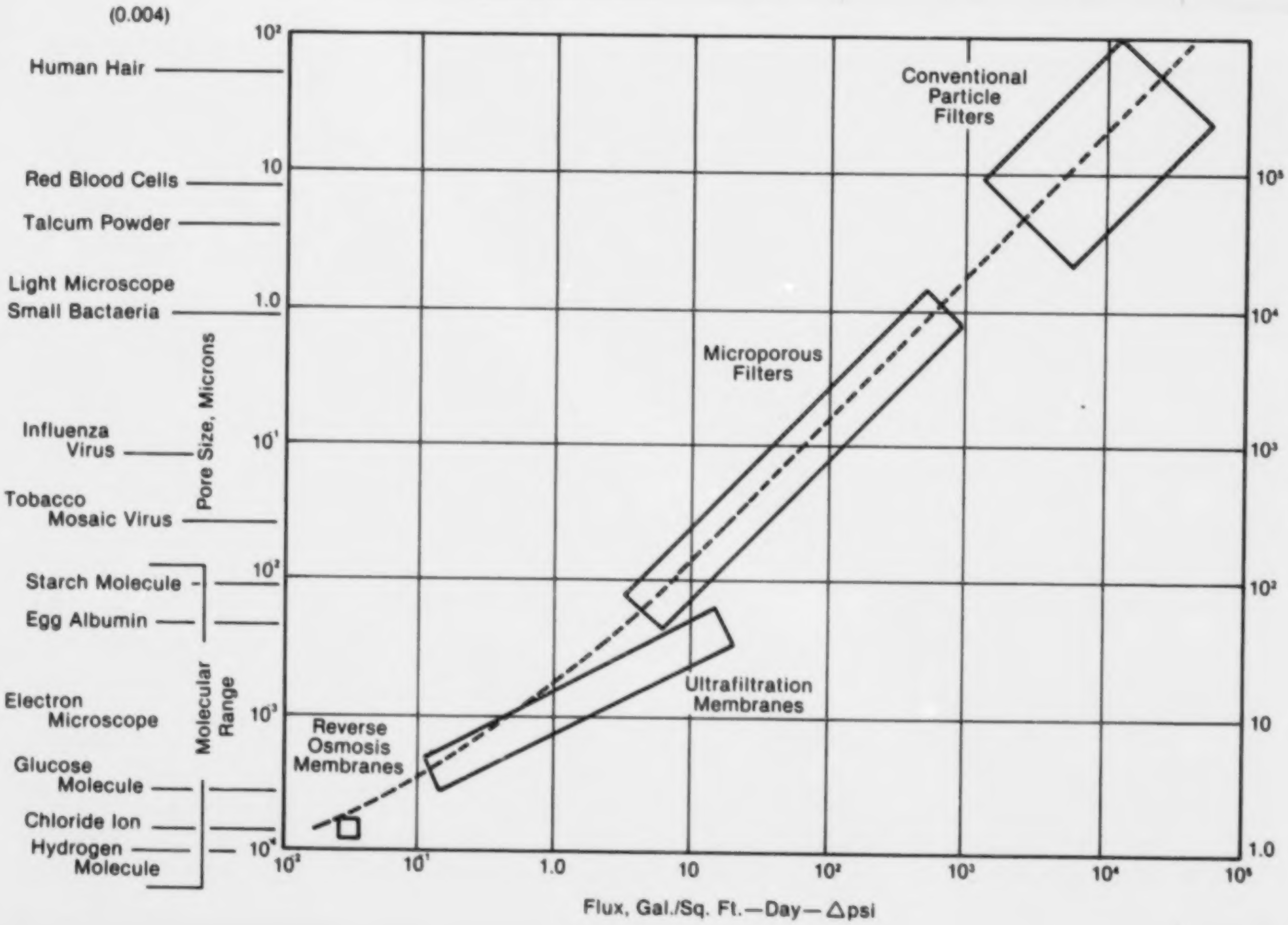

Figure 3. Pore size vs. flux for filtration processes (1).

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Figure 4 presents the effects of operating parameters on the UF flux for concentrating cheese whey. The solvent flux across the UF membrane surface is given by the following equation:

$$J = KP/t \tag{5.1}$$

where J = solvent flux, g/cm^2 sec
K = membrane permeability coefficient, g/cm/sec/atm
P = pressure difference across the membrane, atm
t = membrane thickness, cm

As expected, in the case of pure water (Figure 4a) the flux varies nearly in proportion to the applied pressure. For the "cheese whey", however, the flux increases at low pressures and reaches a plateau at a pressure of about 1.5 kg/cm^2. This phenomenon is caused by "concentration polarization" involving formation of a solute "gel layer" at the membrane surface as the solution becomes more concentrated. This "gel layer" acts as a secondary membrane that offers additional resistance to the solvent flux of the membrane system.

The effect of waste concentration, feed velocity, and temperature on the ultrafiltration flux is illustrated in Figures 4b, 4c, and 4d, respectively. As shown in Figure 4b, the flux declines initially with an increase in feed concentration and levels off at higher solute concentrations. The initial decline in the flux is caused by the concentration polarization effect mentioned above; the flux reaches a constant value when the gel layer reaches the maximum width. Figure 4c indicates that the flux increases with the increase in linear feed velocity, presumably because of the reduced polarization at higher velocity. Figure 4d shows the effect of temperature on flux rates. An increase in temperature generally increases the permeability coefficient (see equation 5.1) and thus the flux.

Types of Membrane Modules

Membranes that can be designed for specific applications are usually fabricated in flat sheets, plates, or tubular forms and are assembled into modules. As with the reverse osmosis process, common module configurations are tubular, spiral wound, and hollow fibers. The advantages and disadvantages of these modules configurations are discussed in Section 4. Key features of some commercial module designs are presented in Table 7.

PROCESS APPLICATIONS AND RELATED STUDIES

Commercial Scale Municipal/Industrial Applications

To date, nearly all commercial uses of the UF process have been in separating and concentrating macromolecules from dilute solutions in industrial applications. There are full scale UF operations in the food processing industry (to concentrate cheese whey), textile industry (to concentrate dye rinses), and in metal cutting and related industries (to concentrate emulsified oils). Recently, UF has also been used in the electronic industry for treating plating rinses and as a post-treatment to ion exchange for raw water treatment.

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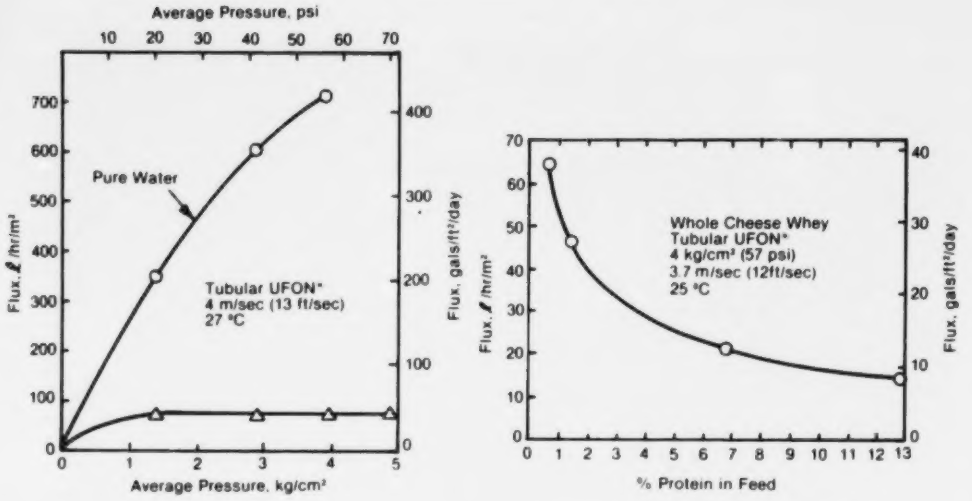
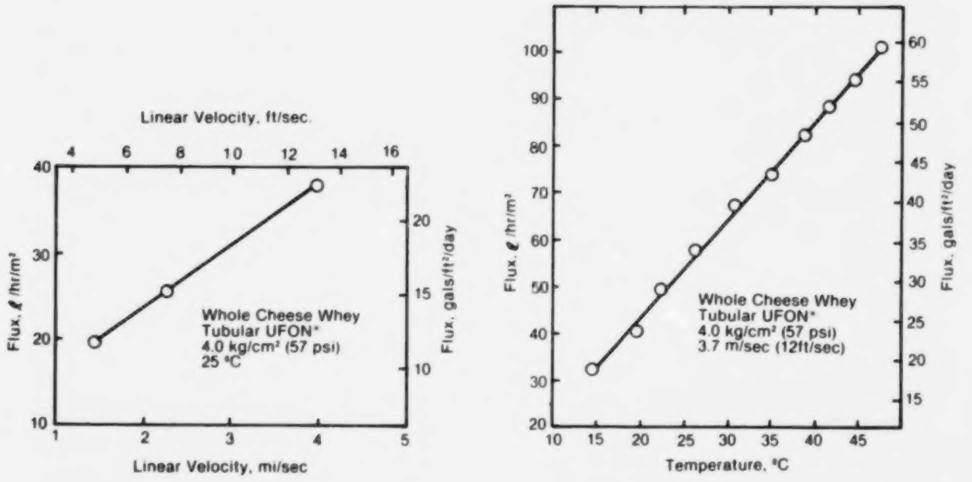


a. Pressure Effect on Ultrafiltration Flux

b. Effect of Concentration on Ultrafiltration Flux



c. Effect of Feed Velocity on Ultrafiltration Flux

d. Effect of Temperature on Ultrafiltration Flux

Figure 4. Effect of operating parameter on UF flux (4).

TABLE 7. FEATURES OF COMMERCIAL UF MODULE DESIGNS*

Company	Geometry	Membrane type
Abcor	1" diameter tubular membranes and spiral wound flat membranes	Originally cellulose acetate; now, other materials that are pH and temperature resistant
Door Oliver	Multiple flat plate	Polyelectrolyte complex (developed by Amicon)
Romicon†	Narrow channel tubular (flat sheet membrane); also hollow fibers	Dynel^R (acrylic), cellulose acetate, Nomex^R (nylon) polyelectrolyte complexes, others
Union Carbide	1/4" tubes	Zirconium oxide on carbon
Millipore	Multiple plate and screen cartridge	Cellulose acetate and other more solvent resistant materials
Osmonics	Spiral wound modules, 2" and 4" diameter	Cellulose acetate and polyarylsulfone
Selas	Tubular	Zirconium oxide deposited in-situ on porous ceramic
UOP	Tubular	Cellulose acetate
Envirogenics	Spiral wound	Cellulose acetate

*Based on data from Reference 1.

†Joint venture of Rohm & Haas and Amicon.

There is little operating data on the UF units used in these and other industrial/municipal applications.

Pilot/Laboratory Scale Studies

In addition to the actual industrial process/wastewater applications mentioned above, a number of engineering/pilot plant studies have been conducted or are currently in progress to assess the applicability of UF to the treatment of other industrial process streams and wastewaters. Results of some of the most pertinent of these studies are summarized in Table 8. The data indicate that the process is very effective in concentrating protein, color, oil, and COD in wastewaters. In treating cheese whey, lactose and salts are essentially unaffected by the process because of their small sizes. Based on the data in Table 8, when used for the treatment of very concentrated wastes, UF permeates (treated effluents) may not meet certain effluent discharge requirements without additional treatment (for example, biological treatment or RO).

Mobile Unit Applications

Most UF manufacturing companies have skid-mounted pilot units that can be installed on a trailer for field pilot studies. These units usually consist of one or two modules having capabilities from about 18,900 ℓ/day to 39,800 ℓ/day (or 5,000 to 10,000 gpd)*.

USE OF UF IN MOBILE UNITS FOR TREATMENT OF WASTE SPILLS

This section evaluates the feasibility of using UF in a mobile unit to treat concentrated waste spills, based on the general requirements discussed in Section 3.

Pertinent Features of UF for Use in Mobile Units

Essentially all key requirements for mobile unit application (see Section 3) would be met by UF. UF units are compact, are commercially available, can be started up and shut down relatively quickly, can be serviced conveniently, would generally produce only a small volume of residue, would not require skilled labor for operation, and can be operated with the electric power produced by a diesel generator. The UF process would be suitable for the treatment of emulsified oil and humic acids and can be used as a pretreatment to RO or other processes for the removal of colloidal substances and high molecular weight organics. Based on the above discussion, the primary limitations of the UF are inapplicability to wastes containing low molecular weight substances and for producing low concentration permeates from highly concentrated wastes.

As discussed earlier, UF is a commercial process, is offered by a number of manufacturers (see Table 7), and has been used in mobile water treatment

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*Telephone communication with Gerald Alexander, Permutit Company, Glendale, CA, February 20, 1979.

TABLE 8. RESULTS FROM UF PILOT/LABORATORY SCALE STUDIES

Stream	Characteristics	Feed	Concentrate	Permeate	Reference
Kraft black liquid	Total solids, ppm	25,000	250,000	5,000	5
	Color, ppm	9,500	94,200	7,000	
Oil coolant	Total solids, ppm	46,300	331,000	5,400	5
	Freon extractable oil, ppm	36,900	320,000	300	
Screen room effluent	Total solids, ppm	2,900	30,100	1,600	5
	Color, ppm	2,000	25,000	150	
	Chemical oxygen demand	2,300	41,300	860	
Cheese whey	Percent protein	0.65	13.1	0.2	4
	Percent lactose	5.0	4.92	5.03	
	Percent salts	0.70	0.79	0.69	
Laundry wastewater	COD, ppm	---	1,950	193	4
Textile sizing (PVS) wastewater	Percent solids	---	4.00	0.68	4

applications. The unit is fairly compact; a 18,900 ℓ/day (5,000 gpd) product water capacity unit using the spiral wound module design would weight about 3.6 kg (8 lb) and would be approximately 10 cm (4 in) in diameter and 100 cm (40 in) in length. The start-up and shut-down of UF consist primarily of turning on-and-off of the high pressure pump and adjusting the pressure gauges. UF modules are connected in series or in parallel with provisions for flow by-pass so that a single module can be by-passed for maintenance service. Operation of UF units does not require highly skilled labor; the operating effort would be limited to turning valves, reading gauges, and collecting samples for chemical analysis. In mobile unit applications, the system would be equipped with on-line monitors for continuous measurement of pH, temperature, pressure, etc. Ordinarily no more than 6 to 12 operator-hours would be required for a 24-hour operation of a UF unit. For safety reasons, however, operation of a mobile unit in the field may require a minimum of 2 persons. The power for the operation can be provided by a diesel electric generator that can be housed in the same mobile unit.

As with any wastewater treatment system, UF produces a residue (reject) that requires disposal. The volume of this reject (waste concentrate) is usually about 10 to 25 percent of the volume of feed water. In field applications, the reject may be collected in drums and subsequently transported to hazardous waste management facilities or municipal sewage treatment plants for further treatment/disposal.

As with all membrane processes, UF units are susceptible to membrane fouling and deterioration. However, the magnitude of the fouling problem is not nearly as big as with RO. When the membrane is fouled to an "unacceptable" level, the unit is taken off service and is cleaned by flushing with detergents or water (this is similar to ordinary sand filtration where the filter is backwashed periodically to remove suspended solids trapped in the filter media). Fouling by the growth of biomass on the membrane surface can be minimized by prechlorination of the waste or periodic flushing of the system with 1 percent formaldehyde.

Engineering Evaluation and Cost Estimates

Based on data obtained from one UF manufacturer*, a preliminary design has been developed for a 227,000 ℓ/day (60,000 gpd) spiral wound UF unit for use on a trailer flatbed. The system, which consists of nine pressure vessels, can be mounted on two heavy skids. Each vessel contains 2 modules. Excluding the pretreatment equipment, the system would have dimensions of 5 m long, 1 m wide, and 1.7 m high (15 ft x 3 ft x 5 ft), would weigh about 680 kg (1,200 lb), and would occupy 8.5 m^3 (225 ft^3) of space. The water recovery is estimated at close to 100 percent. Other components of the system include a high pressure pump, valves and piping, instrument panel, and the power supply source. Power can be supplied to the unit using a diesel electric generator. The generator, a 5 kw unit, would have the approximate dimensions of 2 m (1) x 0.8 m (w) x 1.1 m (h) (6 ft x 2 ft x 3.5 ft), would weigh approximately 900 kg (2,000 lb), and would occupy a volume of 1.8 m^3 (42 ft^3). A storage tank having a volume of about 1.9 m^3 (500 gal) would supply the fuel to the unit.

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*Telephone communication with R. Gibbons, Envirogenics Company, El Monte, CA, April 17, 1979.

The major logistics support required in field applications relate to possible requirements for membrane replacement and sufficient supply of treatment chemicals (acid, base, scale inhibitors, etc.). Under normal operation, it is unlikely that membrane replacement would be required during short-term field operation. In industrial applications, a membrane life of 2 to 3 years has been reported for continuous operation. Assuming a requirement for replacement of 50 percent of the modules during a field application, the volume of the spare modules that may have to be carried on-board is about 0.24 m^3 (8.7 ft^3).

Chemical requirements are determined by the characteristics of a specific waste spill. The quantity of the chemicals which may have to be carried on-board for short-term field operation would be relatively small. For extended field operation, the mobile unit may have to be resupplied with chemicals on an as necessary basis.

The estimated total capital costs for the 227,000 ℓ/day (60,000 gpd) UF unit* and the accompanying diesel electric generator† are estimated at $30,000 and $5,000, respectively. The cost for the UF unit includes cost for UF modules, piping, valves, pressure pump, chemical storage tank, chemical feed pumps, and the instrumentation panel. The cost also covers the engineering and installation fees.

The operating cost for the mobile UF unit per unit volume of waste treated should vary depending on the specific application (for example, waste characteristics, waste volume, chemicals requirement, location of the spill, etc.). Assuming that in most field applications the mobile unit will have to be powered by a diesel electric generator, the fuel for the generator would constitute one of the major items of operating cost. A 5 kw diesel generator would consume about 3 ℓ/hr (1 gal/hr) of fuel† (about $0.70/hr).

REFERENCES

1. Arthur D. Little Co. Physical, Chemical, and Biological Treatment Techniques for Industrial Wastes, EPA Office of Solid Waste Management Programs, PB-275-287, 1976.

2. Bansal, I.K. Progress in Developing Membrane Systems for Treatment of Forest Products and Food Processing Effluents, Water-1976: I. Physical, Chemical Wastewater Treatment, AIChE Symposium Series, No. 166, Vol. 73, 1977.

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*Telephone communication with R. Gibbons, Envirogenics Company, El Monte, CA, April 17, 1979.

†Telephone communication with L. Anderson, Anderson-Belviar Company, Long Beach, CA, January 31, 1979.

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3. Weber, W.J., Jr. Physicochemical Processes for Water Quality Control, Wiley-Interscience, New York, 1972.

4. Envirogenics Systems Company. Membrane Ultrafiltration for Water Treatment.

5. Bansal, I.K. Reverse Osmosis and Ultrafiltration of Oily and Pulping Effluents, Industrial Waste, May/June, 1977, p. 32.

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SECTION 6

ION EXCHANGE

PROCESS DESCRIPTION

Process Principle

Ion exchange is a process whereby the toxic or undesirable ions in a wastewater are exchanged with relatively harmless ions, such as H^+, OH^-, Na^+, HCO_3^-, Cl^-, held by the ion exchange material (usually an organic matrix). The process is used for water softening (removal of Ca^{++} and Mg^{++} hardness), treatment of wastewaters, and for concentration and recovery of ionic substances. The exchange reaction is reversible and concentration dependent, thus making it possible to regenerate the exchange resins for reuse. The exchange reactions can be represented by the following equations:

$$\text{Cation exchange} \quad n(R^-)B^+ + A^{n+} \underset{\text{regeneration}}{\overset{\text{service}}{\rightleftharpoons}} (R^-)_n A^{++} + nB^+ \tag{6.1}$$

$$\text{Anion exchange} \quad n(R^+)D^- + C^{n-} \underset{\text{regeneration}}{\overset{\text{service}}{\rightleftharpoons}} (R^+)_n C^{n-} + nD^- \tag{6.2}$$

where R = ion exchange resin matrix
A^{n+}, C^{n-} = cation and anion to be removed from solution
B^+, D^- = exchangeable ions on the resin matrix

Certain natural substances (for example, natural zeolite, clay, protein) exhibit ion exchange properties, and some (for example, natural zeolite) have been used in water purification. Modern ion exchange resins, however, are primarily synthetic organic materials containing ionic functional groups ($-COO^-$, $-NH_3^+$, $-SO_3^-$, etc.) to which exchangeable ions are "attached". These synthetic resins are structurally stable (that is, can tolerate a range of temperatures and pH conditions), exhibit a high exchange capacity, and can be "tailored" to show selectivity toward specific ions.

Recent advances in synthetic resin technology include the development of "sorptive" (or macroporous) resins capable of removing organics from aqueous systems. The removal mechanism is generally considered to be one of sorption rather than ion exchange; the resin regeneration consists of "elution" of the adsorbed material with an organic solvent or an inorganic salt solution.

Sorptive resins have been used for the removal of phenols (1), alkylbenzensulfonate (ABS) (2), and viruses (3) from waters, and for the treatment of municipal and industrial wastewaters (4-7).

Process Design

Ion exchange resins used for water and wastewater treatment are commonly employed in columnar beds through which the aqueous phase is passed in an upflow or downflow direction. The operation consists of four steps: exchange (service), backwashing, regeneration, and rinsing. In the fixed-bed downflow design, raw water is introduced through the top distributor, and the treated water is collected at the bottom. When the bed is exhausted ("breakthrough" occurs), the feed water flow is stopped, and the bed is backwashed (to remove particulates trapped in the bed). The exhausted resin is then regenerated using an appropriate regenerant. Regenerants most commonly used include brine, hydrochloric acid, sulfuric acid, sodium hydroxide, sodium carbonate, and ammonium hydroxide. In general, one to four bed volumes of regenerants (5 to 10 percent concentration) are used in the regeneration step. The regeneration is followed by a rinse step whereby the excess regenerant is removed from the bed before the bed is returned to service. The spent regenerant is concentrated in substances removed from the wastewater and requires disposal.

To insure long service life and lower operating costs, pretreatment of wastewaters to remove suspended solids is generally necessary prior to ion exchange treatment. Pretreatment may consist of filtration for the removal of suspended solids or activated carbon adsorption for the removal of organics, which may foul a strong base anion resin. Sorptive resins have also been used in a pretreatment step to remove organics and thus reduce the potential for organic "fouling".

Three types of ion exchange systems are in use today. These are cocurrent fixed bed ion exchange, countercurrent fixed bed ion exchange, and continuous countercurrent ion exchange. Brief descriptions of each system, including their advantages and disadvantages, are presented in Table 9.

PROCESS APPLICATIONS AND RELATED STUDIES

Commercial Scale Municipal/Industrial Applications

Ion exchange is widely used in the treatment of municipal and industrial water supplies for hardness removal and demineralization. More recent applications have been in connection with wastewater treatment for water reuse and by-product recovery. Ion exchange has been successfully used to recover chromium from electroplating wastewaters (9) and mercury from chlor-alkai plant effluent (10). An ion exchange system has been installed at an ammunition plant for acid waste demineralization*. Ion exchange has also been used for the treatment of refinery sour waters (11) and radioactive wastes at nuclear power plants*. Use of ion exchange for full-scale application to the

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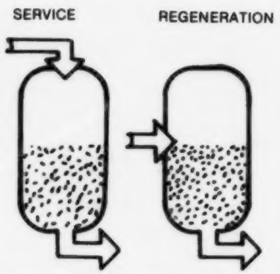
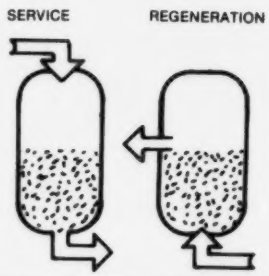
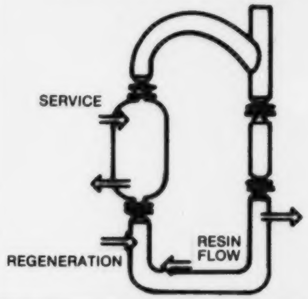
*Information provided by Chemical Separations Corporation, Oak Ridge, TN.

TABLE 9. PERTINENT FEATURES OF ION EXCHANGE SYSTEMS (8)

Types	Cocurrent Fixed Bed  	Countercurrent Fixed Bed  	Continuous Countercurrent 
Description of Process	Downflow of raw fluid to be treated (loading phase). Upflow backwash. Downflow regeneration. Downflow rinse. Batch loading and regeneration.	Regeneration flows opposite in direction to influent. Backwash (in regeneration) does not occur on every cycle to preserve resin stage heights. Resin bed is locked in place during regeneration.	Multi-stage countercurrent movement of resin in closed loop providing simultaneous treatment, regeneration, backwash and rinse. Operation is only interrupted for momentary resin pulse.
Indications for Use	Low loads (200 PPM in softening; 250 TDS in demin). Lower thruput (about 1000 GPM). Where regeneration chemical cost is not critical, disposal of waste volume in large single batch not critical, and dilution of feed no problem. Manual operation acceptable.	Handles high loads at moderate thruput or low loads at high thruput (GPM x TDS or GPM x PPM removal = 40,000 or more). Where effluent quality must be relatively constant, regeneration cost is relatively critical, disposal of single batch waste volume no problem.	Highloads with high thruputs (GPM x TDS or GPM x PPM removal = 40,000 or more). Where constant effluent quality is essential, regeneration costs critical, total waste volume requires small, concentrated stream to be controllable. Where loss of product thru dilution and waste must be minimized. Where available floor space is limited.
Advantages	Low capital cost. Automatic controls instrumentation optional. Simple, basic type of unit. Easy maintenance.	Moderate capital cost. Can be operated with periodic attention. Moderate regeneration cost. Lesser volume of waste due to less frequent backwash. Consistent effluent quality.	Lowest regeneration cost. Lowest resin inventory. Consistent effluent quality. Highest thruput to floor space. Large capacity units factory preassembled. Concentrated low-volume waste stream. Can handle strong chemical solutions and slurry. Fully automatic operation.
Disadvantages	High regenerant cost. Fluctuating effluent quality. Large single batch waste disposal. High water consumption thru dilution and waste. Requires substantial floor space.	Increased controls and instrumentation, higher cost. Requires mechanism to lock resin bed. Large single batches of waste disposal. Moderate water consmption thru dilution and waste. Requires substantial floor space.	Requires automatic controls and instrumentation, higher capital cost. More headroom required.

demineralization of acid mine drainage, treated municipal wastewaters, and a range of industrial wastewaters have been the subject of a number of investigations (9). Some specific examples of full-scale ion exchange application to the treatment of industrial wastewaters are listed in Table 10.

Pilot and Laboratory Scale Studies

Almost every large-scale application of ion exchange to the treatment of industrial wastewaters has been preceded by laboratory and pilot plant studies aimed at selection of the most suitable resin and development of design criteria (resin quantities and regeneration requirements, optimum hydraulic loading, etc.) and basis for cost estimates. Many of the laboratory and pilot scale studies that are currently in progress (largely by resins manufacturers) are aimed at the development of ion-specific and longer life resins (with minimum susceptability to organic fouling). The investigation of the use of ion exchange resins in new applications (for example, treatment of miscellaneous industrial wastewaters) is a continuous effort that is carried out both by resin manufacturers and environmental engineers in the industry.

Mobile Unit Application

Trailer-mounted ion exchange resin systems have been used for field pilot plant studies. A 276 ℓ/min (70 gpm) mobile unit was used for evaluation of the ion exchange as a tertiary treatment for the polishing of secondary effluent from sewage treatment plants in Richland, Washington; Pomona, California; South Lake Tahoe, California; and Washington, D.C. (9). Rohm and Haas Company (Philadelphia, PA) operated two mobile ion exchange units, one for the evaluation of the treatability of TNT production wastewaters at an Army ammunition plant and another for the evaluation of the treatability of a process wastewater at a naval installation*.

USE OF ION EXCHANGE IN MOBILE UNITS FOR TREATMENT OF WASTE SPILLS

This section evaluates the feasibility of using ion exchange in a mobile unit to treat concentrated waste spills, based on the general requirements discussed earlier.

Pertinent Features of Ion Exchange for Use in Mobile Units

In general, nearly all the requirements discussed for applicability of a system to the treatment of waste spills in a mobile unit would be met by the ion exchange process. Ion exchange units are compact, are commercially available, are easily automated, can be started and shut down relatively quickly, can handle a range of organic and inorganic concentrations (including highly acidic and alkaline wastes), can be serviced conveniently, would produce a small volume of residue that may be suitable for processing for material recovery, would not require skilled field labor for operation, and can be operated with the electric power produced on-site by a diesel generator.

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*Information provided by Rohm and Haas Company, Philadelphia, PA.

TABLE 10. SPECIFIC EXAMPLES OF FULL-SCALE ION EXCHANGE APPLICATION TO INDUSTRIAL WASTEWATER TREATMENT

Application	System description	Performance/specification	Reference
Acid wastewater demineralization at an Army ammunition plant	Two trains fixed bed ion exchange with gravity filter, countercurrent regeneration with HNO_3 or H_2SO_4 of cation units; NH_4OH regeneration of anion units. Recovery of NH_4NO_3 as by-product and water for boiler feed. 2 cation units 10 ft dia., 12 ft high; 2 anion units 9 ft dia., 10 ft high.	310 gpm capacity; reduce TDS from 2,800 ppm to less than 20 ppm.	*
Ammonium nitrate recovery from fertilizer plant wastewater	Several continuous ion exchange resin systems in operation at fertilizer manufacturing plants; ammonium nitrate is recovered from wastewater from reuse.	Capacities vary from 40 gpm to 695 gpm; reduce ammonia from as high as 2,500 ppm to less than 25 ppm.	12
Organic color removal from dyestuff production plant	---	300,000 gpd waste stream; color reduced from 75,000 to 500 APHA units; COD, copper and chromium also reduced.	13
Organics removal from pulp and paper mill effluent	Two large resin sorption systems in operation in Sweden and one system in operation in Japan. The systems in Sweden consist of three resin columns, each containing 20 cubic meters of resins; the system in Japan consists of four columns, each with about 30 cubic meters of resins. The resins are regenerated with a caustic wash followed by a reactivation with an acid stream (e.g., H_2SO_4).	92 to 96 percent color removal achieved (from an initial level of 30,000 to 40,000 units); 80 to 90 percent COD removal and 40 to 60 percent BOD removal also achieved.	13

-Continued-

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*Information provided by Chemical Separations Corporation, Oak Ridge, TN.

TABLE 10. (Continued)

Application	System description	Performance/specification	Reference
Para-nitrophenol (PNP) recovery from parathion manufacturing wastewater	Wastewater (pH=2) is passed through 50 cu ft bed of cross-linked polystyrene adsorbent resin. PNP recovered by regeneration with 2 bed volume of 4 percent NaOH followed by water rinse; recovered sodium PNP recycled to the parathion process; two resin beds used; one in service removing phenol; the other in regeneration or standby; since plant operates only part of the year, resin beds are regenerated and kept wet while idle.	Phenol concentration reduced from 1,000-1,800 ppm to 1-5 ppm.	14
Recovery of phenol from phenolic resin manufacturing waste	A weakly basic macroporous ion exchange resin with a cross-linked polystyrene matrix used for phenol recovery from an aqueous process waste. Methanol (9.4 to 22.4 gal/cu ft of resin) is used for regeneration with the phenol/water/methanol recycled to production process.	Phenol concentration reduced from 1.5-2 percent to less than 120 ppm; higher phenol recovery achieved with higher methanol usage.	14
Brine purification	Acidified brine solution contaminated with phenol is passed through two beds of adsorbent beds in series; lead adsorbent bed is periodically regenerated with 4 percent NaOH at 70°C; after one year of operation, resin condition is essentially unchanged.	Phenol in 20 percent waste brine solution is reduced from 10-150 ppm to less than 0.5 ppm.	14

Ion exchange is a commercial process and is offered by a number of vendors*. The system is fairly compact; a 227,000 ℓ/day (60,000 gpd) system would have two columns, each approximately 2.1 m (7 ft) high and 0.91 m (3 ft) in diameter, and when loaded, weighing approximately 2,500 kg (5,500 lb). The system can be designed for manual or automatic operation. Process startup and shutdown would consist primarily of turning on-and-off the feed pump. For manual operation, the operator must have some familiarity with the process; he will decide when to stop one cycle (for example, service) and start the next (for example, backwash). Manual operation would be more suitable for mobile unit application because of the diversity of wastes that are encountered in spill situations. Ordinarily no more than six to twelve operator-hours would be required for a 24-hour operation of an ion exchange unit. For safety reasons, however, operation of a mobile unit in the field may require a minimum of two persons.

The ion exchange system is not an energy intensive unit. The only energy required is for pumping; this energy can easily be provided by a small diesel electric generator that can be housed in the same trailer.

As with any wastewater treatment system, ion exchange produces a residue (spent regenerant) that requires disposal. The volume of residue as a percent of the feed is dependent on factors such as resin capacity, solution concentration, and regeneration parameters, and is seldom higher than 10 percent. In field applications, the regenerant may be collected in drums and subsequently transported to hazardous waste management facilities for further treatment/disposal, or to a recovery facility if the waste can be economically processed for material recovery.

Engineering Evaluation and Cost Estimates

Based on data obtained from one ion exchange process supplier, a preliminary design has been developed for a 227,000 ℓ/day (60,000 gpd) cocurrent ion exchange system for use on a flatbed trailer. The system consists of six steel tanks each containing 0.69 m^3 (24 ft^3) of resin and measuring 21.1 m (7 ft) in height, 0.91 m (3 ft) in diameter, and weighing 2,500 kg (5,500 lb). Other components of the system include a feed water pump, valves and piping, a tank for storage of processed water for backwashing, and the power supply source. Power required for the system can be supplied by a 5 kw diesel electric generator that would have the approximate dimensions of 2 m (l) x 0.8 m (w) x 1.1 m (h) (6 ft x 2 ft x 3.5 ft), would weight approximately 900 kg (2,000 lb), and would occupy a volume of 1.8 m^3 (42 ft^3).

The proposed ion exchange system can be "prepared" to be operated in any one of the following three ways: (a) as a complete demineralization system for application to waters containing little or no organics; (b) as an adsorption-demineralization combination system for the removal of both inorganic ions and organic substances; and (c) as a sorptive system for the removal of organics (for application to wastewaters containing high organic loading). In the first type of application, three columns will carry cation exchange resins on the H^+ cycle whereas three columns will carry anion exchange resins on the OH^- cycle. The cation and anion exchange columns can be operated in series (to increase service life between regeneration of the lead beds) or in parallel (for maximum hydraulic capacity). The piping arrangement would allow for one or more beds to be taken out for regeneration while the remaining columns would remain in service.

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*Major suppliers of ion exchange systems are: Chemical Separations Corp., Oak Ridge, TN; Crane Co., King of Prussia, PA; Ecodyne, Union, NJ; Illinois Water Treatment, Rockford, IL; Infilco, Richmond, VA; LA Water Treatment Co., Industry, CA; and Permutit, Paramus, NJ.

In the adsorption-demineralization combination arrangement, the two lead columns would carry the adsorptive resins and would act as organic scavengers. The other four columns would contain the anion and cation exchange resins and would be operated similar to the "demineralization only" system described above. In the all sorptive resin system, all columns would be filled with adsorptive resins and would be operated in series or in parallel. By carrying two or more different types of adsorptive resins (for example, "polar" and "non-polar" resins) in the columns, the system can provide capability for the removal of a broad spectrum of organics.

In field applications, the bed regeneration requirement is dictated by the concentration of the substances in the raw wastewater and the selected mode of operation. For an organic adsorption application where five beds may be in service at any one time and a wastewater containing one percent organics such as phenols is to be processed, a service life of about 30 minutes would be expected for the lead column before requiring regeneration.

The major logistics support required for field operation relate to chemicals needed for resin regeneration and possible requirements for resin replacement. Under normal operation, it is unlikely that substantial resin replacement would be required during short-term field operation. In various demineralization applications, a resin life of longer than two years has been reported. For continuous operation, resin loss resulting from regeneration is reported at about one percent per year under ideal conditions and at about 10 percent under normal conditions; specific installations which operate under harsh conditions have reported greater than 50 percent losses*.

Chemical requirements for regeneration are determined by the types of resins used and the characteristics of a specific waste spill. In general, H_2SO_4 is used to regenerate the cationic exchangers and NaOH is used to regenerate the anionic exchangers. Sodium hydroxide or organic solvents such as acetone and methanol are used to regenerate sorptive resins. One to three bed volumes of organic solvents or acid or alkali (5 to 10 percent solutions) are required in each regeneration cycle. For extended field operation, the mobile unit may have to be resupplied with chemicals on an as necessary basis.

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*Letter from Ronald Y. Lawrence, Diamond Shamrock Corp., Redwood City, CA, February 14, 1980.

The estimated total capital costs for the ion exchange system described above is $140,000[*], which includes $5,000[†] for the diesel generator[‡]. The operating cost for the mobile unit per unit volume of spill treated should vary depending on the specific application (for example, waste characteristics, waste volume, regenerant requirement, location of the spill, etc.). The regenerant cost would likely constitute a major element of the operating cost. A total regeneration cost of $58 per cycle has been estimated for the regeneration of one cation exchange and one anion exchange bed with four bed volumes of five percent solutions of HCl and NaOH. This estimated cost assumes chemical costs of $39/MT and $155/MT for HCl (32 percent solution) and NaOH (50 percent solution), respectively (15).

The estimated cost for the regeneration of an adsorption resin with four bed volumes of an eluent is estimated at $42 when the bed is regenerated with five percent NaOH solution, $400 when the bed is regenerated with methanol, and $1,150 when the bed is regenerated with acetone. These estimates assume 42¢/ℓ ($1.60/gal) for acetone and 15¢/ℓ (55¢/gal) for methanol (15) and take no credit for acetone or methanol that could be potentially recovered via distillation of the spent eluents.

REFERENCES

1. Pollio, F.X. and R. Kunin. Sorption of Phenols by Anion Exchange Resins, Environmental Science and Technology, Vol. 1, No. 2, p. 160, Feb. 1967.

2. Hinrichs, R.L. and V.L. Snoeyink. Sorption of Benzenesulfonates by Weak Base Anion Exchange Resins, Water Research, 10, pp 79-87, 1976.

3. Kim, B.R., et al. Adsorption of Organic Compounds by Synthetic Resins, Journal of Water Pollution Control Federation, 48, 120, 1976.

4. Rook, J.J. and S. Evans. Removal of Trihalomethane Precursors From Surface Waters Using Weak Base Resins, Journal of American Water Works Association, 71(9), 520, 1979.

5. Chudyk, W.A., et al. Activated Carbon Versus Resin Adsorption of 2-Methylisoborneol and Chloroform, Journal of American Water Works Association, 71(9), 529, 1979.

6. Brenner, L., et al. Evaluation of the Capacity of Granular Activated Carbon and SAD-2 Resin to Remove Trace Organics from Treated Drinking Water, Environmental Science and Technology, 12(2), 1315, 1978.

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[*] Telephone communication with Gerald Alexander, Permutit Company, Glendale, CA, February 20, 1979.

[†] Telephone communication with L. Anderson, Anderson-Bevier Co., Long Beach, CA, January 31, 1979.

[‡] This cost is for a 6-column system design presented here. A 2-, 3-, or 4-bed system, which would cost about 1/3 to 2/3 as much, can also be used in mobile units; such a system, however, would require more frequent regeneration and does not provide as much operational flexibility as a 6-bed design.

7. Anon, Decolorization of Kraft Pulp Bleaching Effluents Using Amberlite SAD-8 Polymeric Adsorbent, Rohm and Haas Company, Philadelphia, PA, 1971.

8. Ion Exchange Systems, Chemical Separations Corporation, Oak Ridge, TN.

9. Water Purification Associates, Innovative Technologies for Water Pollution Abatement, NTIS PB-247-390, 1975.

10. AKZO IMAZ TMR Process for the Removal of Mercury in Water, AKZO ZOOT Chemie, Netherland.

11. Pollio, F.X., et al. Ion Exchange Resins Treats Sour Water, Oil and Gas Journal, 67, 126, 1967.

12. Brennan, J.F. The Chem-Seps Nitrogen Recovery Process: A Pollution Solution that Works, paper presented at the Fertilizer Institute Environmental Symposium, New Orleans, LA. January 14-16, 1976.

13. Arthur D. Little. Physical, Chemical, and Biological Treatment Techniques for Industrial Wastes, Vol. I, NTIS PB-275-054, 1977.

14. Fox, C.R. Plant Uses Prove Phenol Recovery with Resins, Hydrocarbon Processing, November 1978, pp 269-273.

15. Chemical Marketing Reporter, October 8, 1979.

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SECTION 7

WET AIR OXIDATION

PROCESS DESCRIPTION

Process Principle

Wet air oxidation (WAO), also referred to as the Zimpro process, wet oxidation, wet combustion, and wet incineration, is a process especially suitable for the treatment of high strength or toxic organic wastes or wastes containing an appreciable concentration of non-biodegradable organic matter (as reflected by a high COD/BOD ratio). Zimpro, Inc. (Rothschild, Wisconsin) holds a patent on this process. WAO operates at relatively high temperatures, 200 to 320°C (392 to 608°F) and pressures, 1 to 29 mpa (150 to 4,000 psi), and results in the oxidation of most reduced inorganic and organic compounds to inoccuous inorganic end-products (for example, CO_2, H_2O, $SO_4^=$, etc.).

Compared with the conventional combustion processes that generate air pollutants (for example, NO_x, SO_x, etc.) requiring control, no such pollution problems are associated with WAO (1). Also, since oxidation is carried out in a water environment, waste pretreatment such as sludge dewatering or drying that would be required in conventional combustion would not be necessary.

Figure 5 presents a schematic flow diagram for WAO. The raw waste is pressurized to the system pressure by means of a high pressure positive displacement pump*. Air is then injected into the waste by an air compressor and the mixture is heated in the process heat exchanger by the hot reactor effluent. Depending on influent COD concentration and level of treatment desired, additional heating may be necessary. This supplementary heating is provided by a heater that can be either an electrical or an oil-fired oil heating unit.

In the reactor, the organic or reduced inorganic constituents are oxidized. Being an exothermic reaction, the reaction results in a temperature rise in the reactor. The hot effluent is cooled in the process heat exchanger as previously mentioned and in a final cooler to a discharge temperature of 38 to 60°C (100 to 140°F). The final cooler uses cooling water as a cooling medium. The final step in the process is to reduce the pressure of the oxidized waste by means of the pressure control valve. The pressure control valve

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* If the waste contains very large sized (>6 mm or 0.25 in) particles, such particles must be removed or reduced in size (by use of a "grinder") before pumping.

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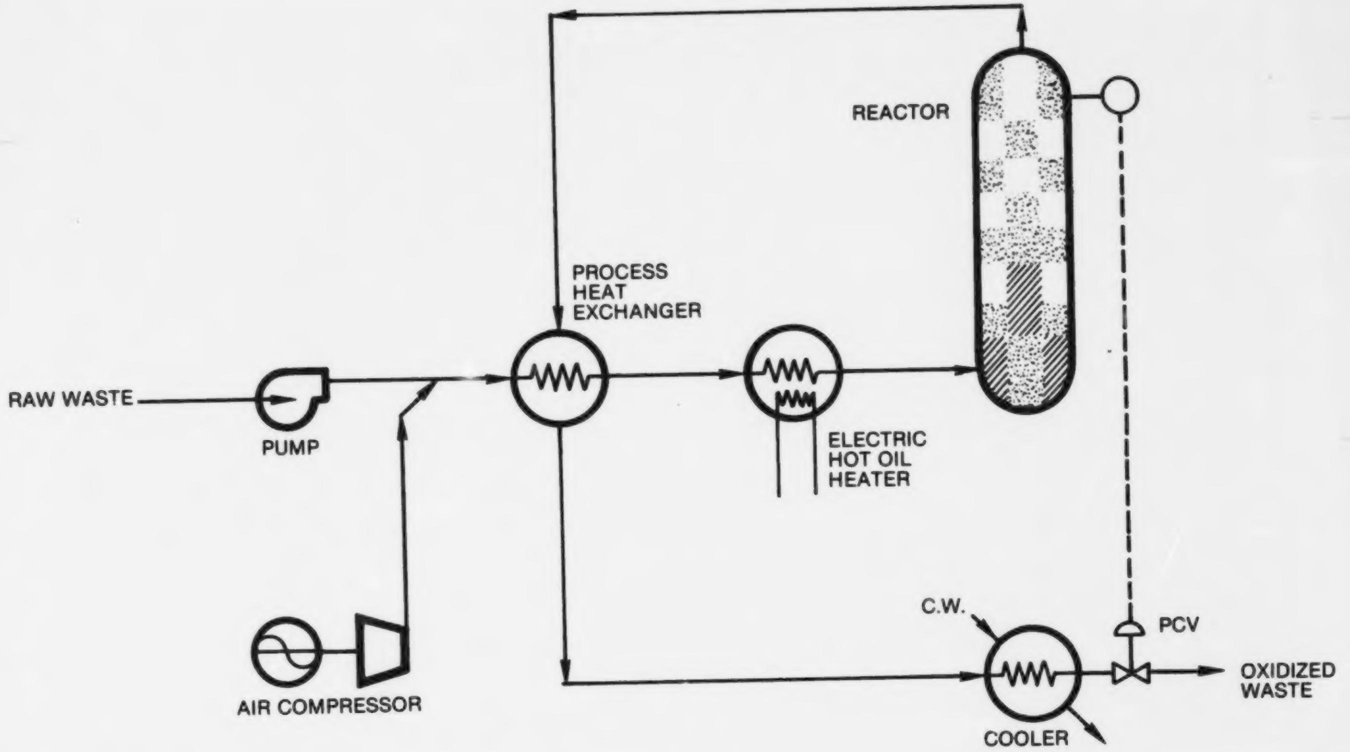
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PUMP
AIR COMPRESSOR
PROCESS
HEAT
EXCHANGER
ELECTRIC
HOT OIL
HEATER
REACTOR
C.W.
COOLER
PCV
OXIDIZED
WASTE

Figure 5. Schematic flow diagram for the WAO process.

maintains the system pressure at a pre-set point. When waste contains appreciable quantities of undesirable inorganic constituents (for example, fluorides, heavy metals, etc.), further treatment of the WAO effluent may be necessary prior to final discharge. In certain applications (for example, treatment of organic sludges to improve dewaterability) where WAO is operated at relatively low temperatures, little destruction of organics is affected. In large-scale applications, the reactor effluent is passed through a gas-liquid "separator" where hot exhaust gases are recovered and used to drive the air compressors. The exhaust gas, which may contain volatile organic matter, would be treated before final discharge. In mobile spill waste treatment applications, where complete oxidation of organics is desired, WAO reactor would be operated at very high temperatures and the exhaust, which would consist primarily of steam, CO_2, and N_2 (from the air supply), would not require separation and treatment. For such small scale application it would also not be economical to use the effluent steam to power the air compressor.

Process Control Parameters

By proper selection of operating parameters, any degree of oxidation (including complete destruction) of reduced organic and inorganic waste constituents can be achieved. Operating parameters that affect oxidation efficiency are temperature, detention time, and pressure. The process air input and supplementary heating requirements are determined by the waste characteristics and the selected operating conditions.

The effect of temperature on the oxidation of five concentrated simulated or actual wastes is shown in Figure 6. As noted in the figure, the oxidation efficiency, as indicated by the reduction in COD, generally increases with the rise in temperature. Figure 7 presents typical data on the effect of detention time on oxidation efficiency for several temperatures. The data in this figure indicate that (a) at low temperatures, only partial oxidation of the waste is affected even with very long detention times and (b) at temperatures greater than 200°C (392°F), maximum achievable oxidation is attained in about 30 minutes. Although the oxidation efficiency increases with the rise in temperature, the operating temperature cannot exceed the critical temperature of water (374°C or 905°F) because continuous presence of a liquid phase is essential for oxidation. Operations at high operating temperatures require that the process be run at high pressures in order to avoid complete vaporization of water. Ordinarily, the operating temperature is selected to achieve the desired degree of oxidation for a selected reaction time. If the reaction time is to be short and near complete oxidation is to be achieved (as for mobile spill treatment applications), the system would have to be operated at high temperature and pressure.

The air-to-steam ratio at saturation in the reactor vapor space is given by the following equation (9):

$$\frac{A}{S} = \frac{144\ (P_t - P_s)\ V_s}{53.3\ T} \qquad (7.1)$$

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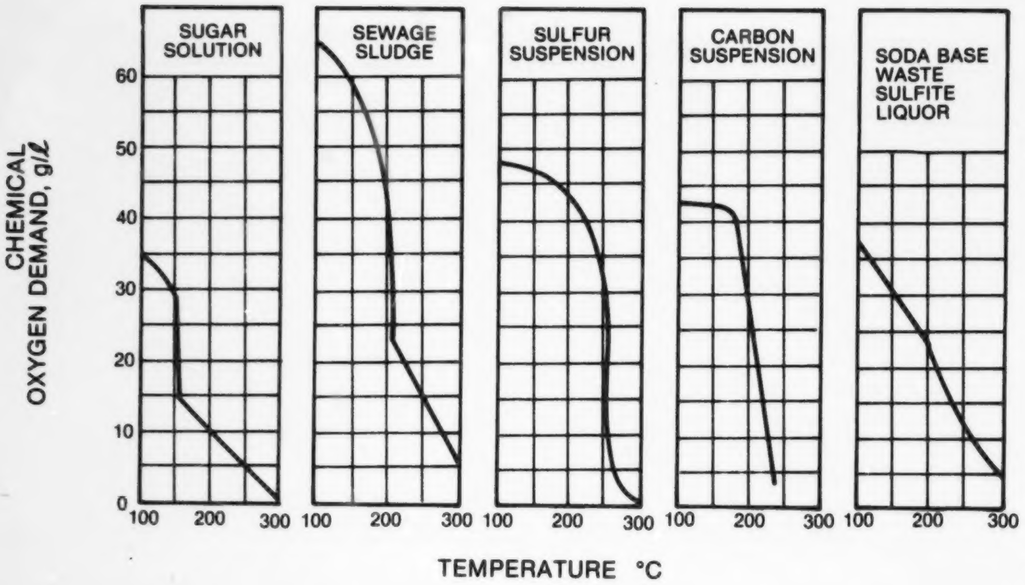

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Figure 6. Oxidation curves for concentrated simulated or actual wastes (2).

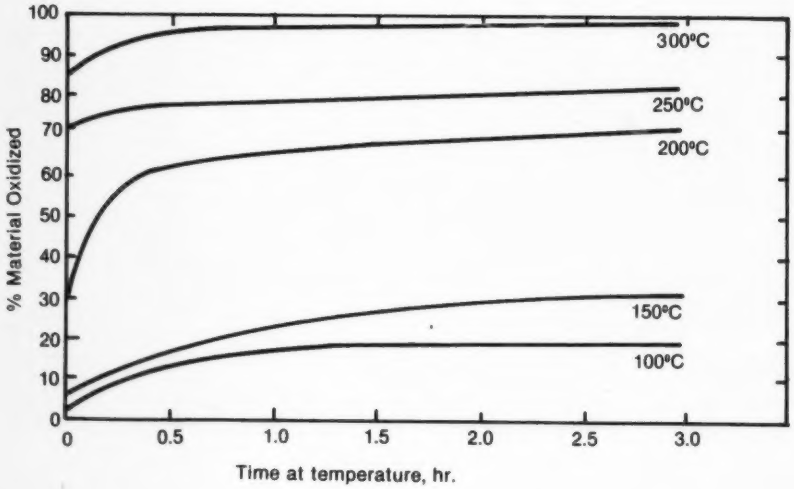

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Figure 7. Time-temperature effect on the degree of oxidation (2).

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where S = steam, lbm
A = air, lbm
T = temperature, PF
P_t = total pressure, psia
P_s = saturated steam pressure, psia
V_s = specific volume of saturated steam, ft^3/lbm

The quantity of air added to the wastewater should be sufficient to achieve oxidation and should not exceed the $\frac{A}{S}$ ratio corresponding to the operating temperature and pressure of the reactor. Higher $\frac{A}{S}$ ratios would result in complete evaporation of the water. If the quantity of air required for a desired level of oxidation exceeds that indicated by the $\frac{A}{S}$ ratio for the selected reactor operating temperature and pressure, the oxidation level that actually would be achieved would be less than that desired. To achieve the desired level, the reactor operating conditions would be adjusted.

Depending on the selected operating temperature and the heating value of the waste, supplementary preheating of the waste may not be required (except for startup). The heating value of the waste is determined by the nature and concentration of the oxidizable waste components. Heating values for selected compounds and waste materials and the theoretical amount of air required for their complete oxidation are presented in Table 11.

PROCESS APPLICATIONS AND RELATED STUDIES

Commercial Scale Municipal/Industrial Applications

There are currently more than 150 WAO units in operation worldwide; about 90 percent of the units handle municipal sludges whereas the remaining 10 percent process industrial wastes (4). In application to municipal sludges, where the objective is to improve sludge characteristics and not to achieve destruction of organics, the units are operated at relatively low temperatures (150 to 200°C or 302 to 392°F). A total sludge processing cost of \$30 to \$40 per tonne of dry solid has been reported for these applications(3).

WAO has been used for the treatment of cyanide wastes, pulp and paper waste liquor (5,6), glue manufacturing (4), and photographic wastes (7). There are at least four plants treating acrylonitrile and coke production effluents for the destruction of cyanides in these wastes (8). In one such application, the cyanide content is reportedly reduced from 200 ppm to 6 ppm, and the COD is reduced from 32 g/ℓ to 8 g/ℓ (4).

Pilot and Laboratory Scale Studies

Based on laboratory test data, WAO is effective in the treatment of a wide variety of wastes. Explosive materials such as nitrocellulose can be safely destroyed by WAO (4). As a pretreatment method, WAO can render certain toxic or non-biodegradable materials (for example, pesticides, plastics, etc.) amenable to biological oxidation (3). Table 12 presents data on WAO efficiency for ten "priority pollutants". As noted in the table, destruction efficiencies of greater than 99.8 percent and 81 percent are achieved at temperatures

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TABLE 11. HEATING VALUES FOR SOME COMPOUNDS AND WASTE MATERIALS AND AIR REQUIREMENTS FOR THEIR OXIDATION (2)

Material	Btu/lb	Lb of O_2/lb of material	Lb of air/lb of material	Btu/lb of air
Hydrogen	61,000	7.937	34.34	1,780
Ethylene	21,460	3.42	14.8	1,450
Carbon	14,093	2.66	11.53	1,220
Acetic acid	6,270	1.07	4.6	1,365
Oxalic acid	1.203	0.178	0.77	1,565
Pyridine	14,950	2.53	10.9	1,370
Fuel oil	19,376	3.26	14.0	1,380
Lactose	7,100	1.13	4.87	1,455
Casein	10,500	1.75	7.55	1,395
Waste materials:				
Waste sulfite liquor solids	7,900	1.32	5.70	1,385
Semi-chemical pulp solids	5,812	0.955	4.13	1,410
Sewage sludge primary	7,820	1,334	5.75	1,365
Sewage sludge activated	6,540	1.191	5.14	1,270

TABLE 12. WAO EFFICIENCY FOR TEN PRIORITY POLLUTANTS (1-HR DETENTION TIME)(9)

Compound	Starting concentration (g/l)	% Starting material destroyed 320°C	% Starting material destroyed 275°C
Acenaphthene	7.0	99.96	99.99
Acrolein	8.41	>99.96*	99.05
Acrylonitrile	8.06	99.91	99.00†
2-Chlorophenol	12.41	99.86	94.96†
2,4-Dimethylphenol	8.22	99.99	99.99
2,4-Dinitrotoluene	10.0	99.88	99.74
1,2-Diphenylhydrazine	5.0	99.98	00.08
4-Nitrophenol	10.0	99.96	99.60
Pentachlorophenol	5.0	99.88	81.96†
Phenol	10.0	99.97	99.77

*The concentration remaining was less than the detection limit of 3 mg/l.

†The % destruction for acrylonitrile, 2-chlorophenol, and pentachlorophenol at 275°C were increased to 99.50, 99.88, and 97.3 by addition of cupric sulfate (catalyst).

of 320°C (608°F) and 275°C (527°F), respectively. Bioassay tests conducted on the raw and treated wastes indicated a 15 to 4,000 fold reduction in toxicity (9).

As noted in Table 12, use of a catalyst can increase the efficiency of WAO for certain substances (thus permitting operation at lower temperatures). Similar results have been reported in laboratory batch studies using 0.001 to 0.005 mole/ℓ of catalysts such as $CuSO_4$, $Fe_2(SO_4)_3$, and H_2O_2(10).

Mobile Unit Applications

Currently there is a WAO mobile unit available for waste treatment. This unit, which is owned and operated by Zimpro Inc., the developer of the process, has a capacity of 23 ℓ/hr (6 gal/hr) and is used for waste treatability demonstration studies (11). Although the trailer-mounted unit can be moved from site-to-site, for economic reasons the unit has been stationed at the company's headquarters in Rothschild, Wisconsin, and wastes for continuous treatability tests are brought to the site in 1,890 ℓ (500 gal) batches. Zimpro has a 2,300 ℓ/hr (10 gpm) mobile unit currently under design which will be mounted on two trailers. An isometric drawing of the unit is presented in Figure 8.

USE IN MOBILE UNITS FOR THE TREATMENT OF WASTE SPILLS

This section evaluates the feasibility of using WAO in a mobile unit to treat concentrated waste spills, based on the general requirements discussed previously.

Pertinent Features of WAO for Use in Mobile Units*

The major limitations of the WAO for mobile unit applications are (a) the relatively small capacity of the units suitable for trailer mounting, (b) special design and material of construction requirements, (c) requirements for skilled labor, and (d) relatively high capital costs.

As noted previously, Zimpro has a 54,000 ℓ/day (14,400 gal/day) unit currently under design. This unit is considered probably the largest capacity unit that can be trailer truck-mounted. The unit, which will be mounted on two trailers, thus will not meet the mobile unit size requirement of a single trailer unit with a capacity of 227,000 ℓ/day (60,000 gal/day); neither of the two Zimpro trailers, however, would exceed the criteria for trailer weight limit.

The WAO unit shown in Figure 8 is expected to be thermally self-sustaining for wastewaters that have a minimum COD of 3,500 mg/ℓ. More dilute wastewaters require supplemental heating from the hot oil system. The WAO trailer unit has been primarily designed for on-site use at a waste generator's manufacturing

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*Most of the technical data presented in this section are those supplied by Zimpro (letter from L.A. Schaefer, Zimpro Inc., Rothschild, WI, March 25, 1980).

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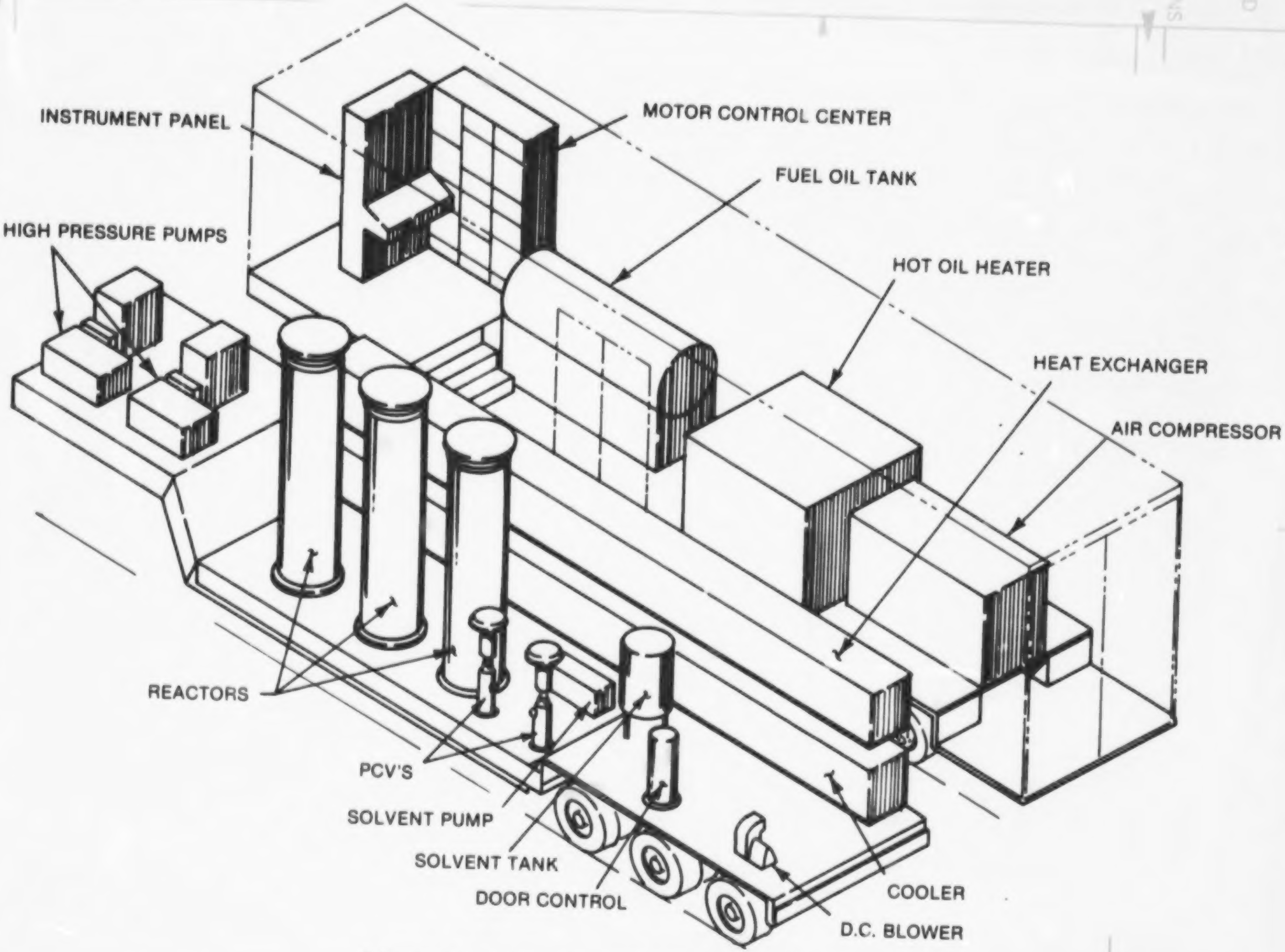
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MOTOR CONTROL CENTER
FUEL OIL TANK
HIGH PRESSURE PUMPS
HOT OIL HEATER
HEAT EXCHANGER
AIR COMPRESSOR
REACTORS
PCV'S
SOLVENT PUMP
SOLVENT TANK
DOOR CONTROL
COOLER
D.C. BLOWER

Figure 8. Wet air oxidation mobile unit.*

*Provided by L.A. Schaefer, Zimpro Inc., Rothschild, WI, March 25, 1980.

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facilities. As a result, an electric generator (200 kw) and cooling water supply (40 gpm) have not been incorporated into the design. Including a generator, however, is not considered to pose a problem. The cooling water could be obtained in an emergency, short term situation from a stream or lake. Failing that, a small self-contained package cooling tower or refrigeration unit could be incorporated into the design.

Although ineffective in handling mineral wastes, WAO is most suitable for treatment and detoxification of organic and oxidizable inorganic wastes. The process does not have the toxicity sensitivity of biological treatment or the very large fuel cost of disposal by incineration. In contrast to other technologies which concentrate the waste to smaller volumes for subsequent disposal to landfills or by incineration, WAO renders the organic wastes innocuous.

To be compatible with the spectrum of wastes (including highly corrosive wastes) anticipated in spill situations, a WAO mobile unit must be designed to enable operation at very high temperatures and pressures and the reactor, heat exchanger, and fluid conduits should be constructed of titanium. Even when titanium is used as the material of construction, potential problems could exist if the pH is less than 2 and chlorides were simultaneously greater than 15 to 20 mg/ℓ. Problems could also exist with fluorides at a pH greater than 7 and highly caustic situations where the pH is greater than 10. Because of its titanium construction, the capital cost of WAO is considerably higher than those of alternative processes (for example, RO).

A mobile WAO unit could be set up and started in twelve hours; once appropriate conversions are made, actual start-up would take about four hours. Even though WAO designs would incorporate a number of safeguards against possible explosions, because of the high temperature and pressure nature of the operation, it is very desirable to have the unit operated by trained personnel. The only requirement for periodic operations and subsequent storage is the need to drain the water from the unit for freeze protection purposes.

Engineering Evaluation and Cost Estimates*

Zimpro has had its 23 ℓ/hr (6 gal/hr) mobile unit available for the last five years, during which time a wide variety of actual industrial wastewaters have been treated. The mobile unit shown in Figure 8 is under design and should be available in 1981. If the waste spill market proves to be a viable one, Zimpro does not anticipate any problems adapting its mobile unit experience to make the minor modifications necessary to be consistent with the guidelines for spill treatment equipment presented in this study. After building 150 WAO units over the last 20 years, Zimpro considers the small mobile units relatively easy to build.

Though the capital cost for a WAO unit is high, the operating cost is low. The capital cost for the mobile unit shown in Figure 8 is around $1.25

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*Based on technical data provided by L.A. Schaefer, Zimpro Inc., Rothschild, WI (letter dated March 25, 1980).

to $1.5 million. This cost includes the costs of a diesel electric power generator and all system components (high pressure displacement pump, air compressor, process heat exchanger, hot oil heater, reactor and final cooler).

The operating costs for a mobile WAO unit would vary somewhat depending on the COD of the wastewater. Assuming that in most field applications, supplementary heating of the waste would be necessary to raise the waste temperature to the desired reactor temperature and that the mobile unit will have to be powered by diesel electric generator, the fuel consumption for the generator would be essentially the only operating cost. A 200 kw generator would consume about 56 ℓ/hr (15 gal/hr) of fuel. This would result in a cost of $15/hr, not including labor, which is approximately 2.5¢ per gallon of waste that is detoxified.

REFERENCES

1. Process Design Manual for Sludge Treatment and Disposal, EPA Report No. 625/1-74-006.

2. Teletzke, G.H. Wet Air Oxidation, Chemical Engineering Progress, Vol. 60, No. 1, p. 33, 1964.

3. Liptak, B.G. Environmental Engineers' Handbook, Vol. 1. Water Pollution, Chilton Book Co., Radnor, PA, 1974.

4. Pradt, L.A. Developments in Wet Air Oxidation, Chemical Engineering Progress, Vol. 68, No. 12, p. 72, 1972.

5. Hoeft, J.E. and C.L. Soukup. Wet Air Oxidation at Ontonagon, paper presented at TAPPI Akaline Pulping Conference, Williamsburg, Virginia, 1975.

6. Morgan, J.E. Innovation in Soda Black Liquor Recovery, presented at TAPPI Non-Wood Plant Fiber Conference, Atlanta, GA, October 1973.

7. Water Purification Associates, Innovative Technologies for Water Pollution Abatement, NTIS Report No. PB-247-390, 1975.

8. PAT Report, Wet Air Oxidation Comes of Ages, Environmental Science and Technology, Vol. 9, No. 4, p. 300, 1975.

9. Randall, T.L. and P.V. Knopp. Detoxification of Specific Organic Substances by Wet Oxidation, paper presented at the 51st Water Pollution Control Federation, Anaheim, Calif., September 1978.

10. Chowdhury, A.K. and L.W. Ross. Catalytic Wet Oxidation of Strong Waste Waters, Water-1975, AIChE Symposium Series, No. 151, Vol. 71, p. 46, 1975.

11. Wilhelmi, A.R. and R.B. Ely. The Treatment of Toxic Industrial Wastewaters by a Two-step Process, presented at 30th Annual Purdue Industrial Waste Conference.

SECTION 8

BIOLOGICAL TREATMENT

PROCESS DESCRIPTION

Process Principle

Biological oxidation involves the use of microorganisms to convert the dissolved and oxidizable organic matter to organic or inorganic end products and to agglomerating microbial flocs (biological sludge) that can be removed subsequently by settling and/or filtration. Biological oxidation can be carried out aerobically (in the presence of dissolved oxygen) or anaerobically (in the absence of dissolved oxygen). The end products of aerobic oxidation are stable gaseous and dissolved inorganics such as carbon dioxide, water, sulfate, and nitrate. The end products of anaerobic decomposition are primarily methane and CO_2 with sulfur-bearing compounds also yielding reduced sulfur species such as mercaptans and hydrogen sulfide. Anaerobic oxidation is considerably slower and less efficient and requires a greater degree of process control than aerobic oxidation. It is primarily used for the stabilization of organic sludges and concentrated organic wastes.

Being biological processes, both aerobic and anaerobic oxidation are unsuitable for the treatment of wastes containing high concentration of toxic substances (for example, heavy metals, phenols) and refractory organics (for example, tertiary butyl alcohol or pyridine), wastes deficient in certain nutrients (for example, primarily nitrogen and phosphorus compounds), wastes having very low or high pH, and wastes that fluctuate widely in chemical composition. Some of these wastes, however, can be made amenable to biological oxidation by proper pretreatment such as nutrient addition, pH adjustment, dilution, extended acclimation, or removal of toxic elements (for example, precipitation of heavy metals).

Process Design Considerations

Aerobic biological treatment systems must be designed to provide for (a) an adequate level of dissolved oxygen in the wastewater, (b) retention of a proper concentration of an active biomass in the biological "reactor" (in relation to the concentration of organics in the feed wastewater (that is, food-to-microorganism ratio), (c) sufficient mixing and contact time in the reactor, and (d) subsequent settling and removal of solids to provide a clarified effluent.

The most widely used biological treatment systems are activated sludge, trickling filters, lagoons (waste stabilization ponds), and oxidation towers. From the standpoint of potential for use in mobile units, activated sludge is probably the most relevant and is the only process considered in this assessment.

The conventional activated sludge process consists of a biological reactor unit containing a high concentration of microorganisms. Air is supplied either by mechanical aeration or by a diffused air system. The treated waste is sent to a clarifier for solids/liquid separation. A portion of the settled sludge is recycled to the biological reactor to "seed" the raw wastewater; the excess sludge is sent to disposal.

A recent advance in the activated sludge process is the development of the high purity oxygen activated sludge process where high purity oxygen is used instead of air for biological oxidation. A considerable saving in capital and operating cost is realized because of higher oxygen utilization efficiency that enables the use of smaller reactors, reduces power consumption, and improves the settleability of the biological flocs. The high purity activated sludge process, developed and marketed by Union Carbide Corporation (New York, NY) as the "UNOX" process and by Air Products and Chemicals, Inc. (Allentown, PA), is currently used in a number of large scale applications involving biological treatment of municipal and industrial wastewaters. Some distinguishing process performance and operating features of the high purity oxygen process include the following:

- Economical operation at high mixed-liquor DO levels (-10 mg/ℓ DO).
- Multistage or plug flow operation at high organic loadings and high MLSS levels without oxygen limitation.
- High volumetric oxygenation capacity per unit of gas-liquid contacting power input.
- Operation under high rate, high MLSS levels with good sludge settleability, compactability, and low sludge recycle rations.
- Low sludge production under low retention time, high organic loading conditions.

Table 13 compares the process design conditions for the high purity oxygen system and for the conventional air activated sludge process for typical municipal wastewater.

The high purity oxygen system, which appears to be a suitable biological oxidation process for use in mobile units, is briefly reviewed in the following section.

The High Purity Oxygen Activated Sludge Process Description

Figure 9 is a schematic diagram of the high purity system. The reactor tank is divided into several essentially identical sections or stages by means

TABLE 13. COMPARISON OF PROCESS DESIGN CONDITIONS FOR THE HIGH PURITY OXYGEN SYSTEM AND FOR CONVENTIONAL AIR AERATION SYSTEMS FOR TYPICAL MUNICIPAL WASTEWATER (1)

Parameter	UNOX oxygenation system	Conventional air aeration systems
Mixed-liquor DO level - mg/ℓ	6 - 10	1 - 2
Aeration detention time (raw flow only) - hours	1 - 2	3 - 6
MLSS concentration - mg/ℓ	6,000 - 10,000	1,500 - 4,000
MLVSS concentration - mg/ℓ	3,900 - 6,500	900 - 2,600
Volumetric organic loading - lbs BOD/day/1,000 cu ft	150 - 200	30 - 60
Food biomass ratio - lbs BOD/lb MLVSS	0.4 - 0.8	0.3 - 0.6
Recycle sludge ratio - lbs recycle/lb feed	0.2 - 0.4	0.3 - 1.0
Recycle sludge concentration - mg/ℓ	20,000 - 40,000	5,000 - 15,000
Sludge volume index (Mohlman)	30 - 50	100 - 150
Sludge production - lbs VSS/lb BOD removed	0.3 - 0.45	0.5 - 0.75

of baffles and is covered with an air-tight lid. High purity (90-100 percent by volume) oxygen gas is fed into the first stage at a pressure of about 2.5 to 10 cm (4 in) of water column above ambient. Feed wastewater and recycled sludge are also introduced into the first stage. The liquid and gas phases then flow concurrently through the system.

The successive aeration stages are connected to each other with only a slight pressure drop between stages. This allows the gas to flow freely from one stage to the next, but prevents backmixing or interstage mixing of the aeration gas. Within a given stage, gas is recirculated at a rate usually higher than the rate of gas flow from one stage to another. As a higher proportion of the oxygen demand is met in the initial stages, the volume of gas required to maintain the desired dissolved oxygen level in the mixed-liquor will be lower in the second and third stages than in the first stage.

Mass transfer and mixing within each stage is accomplished either with surface aerators or with a submerged-turbine rotating-sparge system. In the

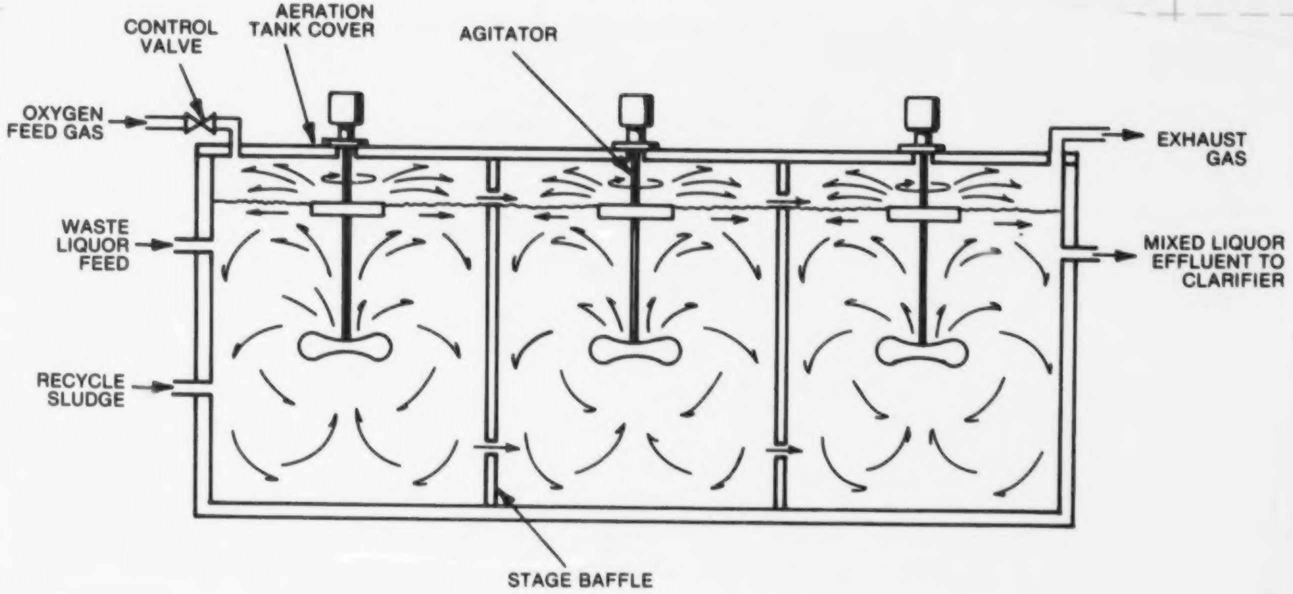
CONTROL VALVE
AERATION TANK COVER
AGITATOR
OXYGEN FEED GAS
EXHAUST GAS
WASTE LIQUOR FEED
MIXED LIQUOR EFFLUENT TO CLARIFIER
RECYCLE SLUDGE
STAGE BAFFLE

Figure 9. Schematic diagram of high purity oxygen system (1).

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first case, mass transfer occurs in the gas space; in the latter, gas is sparged into the mixed-liquor where mass transfer occurs from the gas bubbles to the bulk liquid. In both cases, the mass-transfer process is enhanced by the high oxygen partial pressure maintained under the tank covers in each stage.

Since the oxygen gas fed to the system is devoid of nearly all nitrogen, and since approximately 90 percent of the oxygen gas normally is used, the total gas venting from the system is relatively small. Since the reactors are covered, gas is vented at a single point, thus allowing for effective control of odor and biological aerosols.

Process control for this system is relatively simple. A small positive pressure is maintained by the feed gas flow controller. As the organic load and respiration (oxygen demand) of the biomass increases, the pressure tends to decrease and feed oxygen flow into the system increases to re-establish the pressure set point of the controller. Feed oxygen to the multiples system can be controlled on this pressure demand basis by a simple regulator, or differential pressure controller, automatic valve compilation.

Sludge separation and oxygen supply can be achieved by conventional means. Oxygen can be generated on-site, although for a mobile treatment unit, purchased liquid oxygen would probably be more economical. For large applications, oxygen is generated on-site from air by the cryogenic air separation process or by the pressure-swing adsorption process. In mobile unit applications, oxygen can be supplied from a liquid oxygen supply tank. Sludge separation and effluent clarification can be achieved using conventional gravity settling and/or filtration.

PROCESS APPLICATIONS AND RELATED STUDIES

Commercial Scale Municipal/Industrial Applications

The high purity oxygen process was first given a full-scale demonstration in 1968 at Batavia, NY, by Union Carbide (2). Since that time there have been numerous full-scale municipal and industrial applications of the process. The process has partially or completely replaced conventional air activated sludge at a number of municipal wastewater treatment plants (3). It has also been successfully used to treat industrial wastes including brewery waste, citrus waste, and wastewater from a chemical plant producing silicone based products. Table 14 summarizes some data on these applications. Full-scale process designs have also been proposed for Kraft mill effluent (4) as a result of successful pilot plant programs. A 5.67-million liter per day (1.5 mgd) plant treating high strength citrus waste has been in operation in California since 1976*. The plant handles average raw wastewater COD and suspended solids concentrations of 9,500 ppm and 4,000 ppm, respectively, and produces an effluent with a COD of 300 to 400 ppm and a suspended solids concentration of 50 to

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*Letter from Keith H. Conarroe, Sunkist Growers, Inc., Corona, CA, November 1979.

TABLE 14. THE HIGH PURITY OXYGEN SYSTEM PERFORMANCE IN FULL-SCALE APPLICATIONS

Wastewater	Influent characteristics, mg/ℓ				Percent Removal				Reference
	BOD	COD	TSS	TOC	BOD	COD	TSS	TOC	
Brewery waste	1,632	2,844	536	-	97	94	88	-	5
Municipal sewage	136 - 240	290 - 365	101 - 159	90 - 110	81 - 94	72 - 83	79 - 92	50 - 81	6
Silicon chemical plant	425	595	-	-	95	-	-	-	7
Citrus waste	-	9,500	4,000	-	-	96	98	-	*

*Letter from Keith H. Conarroe, Sunkist Growers, Inc., Corona, CA, November 1979.

100 ppm. Because of the low pH and nutrient deficiency of the wastewater, ammonium hydroxide and phosphoric acid are added to the raw wastewater. The reactor carries a MLVSS concentration of 5,100 ppm and is operated at a detention time of 37 hours and a DO level of 6 to 10 ppm. When first started and proper "seed" was unavailable, it took about two weeks to achieve full, stable operation.

Pilot and Laboratory Scale Studies

By 1973 over 40 municipal and industrial plants had used mobile high purity oxygen pilot plants to test the feasibility of using an oxygen activated sludge system to treat their wastewater. Representative industries whose wastewaters were treated include petrochemical, Kraft mill pulp and paper, pharmaceutical, brewery and food processing, meat packing, grain, cereal, syrup processing, textile, poultry processing, fruit canneries, and mixed industrial operations (8). Typical results obtained in some of these pilot plant operations are shown in Table 15.

High purity oxygen activated sludge has been tested on industrial wastewaters containing as high as 9,500 ppm of COD (see Table 14). Application to high concentration wastes, however, has required a very long detention time to achieve high levels of organics removal. Air Products and Chemicals reports having treated an industrial wastewater containing 2,500 ppm BOD_5 with a detention time of 20 to 25 hours*. The Union Carbide UNOX system has been pilot tested on a chemical plant wastewater containing 3,000 ppm BOD_5; a BOD_5 removal efficiency of 90 to 95 percent was obtained when the system was operated with a detention time of 10 to 12 hours†. UNOX process has been pilot tested for the treatment of diluted coal conversion wastewater. The wastewater (see Table 16 for typical composition) was diluted 1:19 with river water and treated at an organic loading of 0.54 kg BOD_5/day/kg of MLVSS using a detention time of 19.6 hours and a MLVSS of 3,800 mg/ℓ in the aeration tank. The results obtained are summarized in Table 17.

Mobile Unit Applications

Air Products and Chemicals, Inc. and Union Carbide Corporation operate mobile, high purity oxygen, activated sludge process pilot plants that are used for wastewater treatability studies. These pilot plants have a hydraulic capacity of 15 to 23 ℓ/min (4 to 6 gpm). The majority of pilot plant studies using the UNOX process have been carried out in mobile pilot plant units supplied by Union Carbide Corporation. Union Carbide presently has seven mobile pilot plants available for UNOX wastewater treatment studies†. These pilot plants, which have a hydraulic capacity of approximately 19 to 151 ℓ/min (5 to 40 gpm), are contained within 12 m (40 ft) van trailers and include an external clarifier (see Figure 10). The van includes a 6,048 ℓ

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[*] Letter from Roy Lagslet, Air Products and Chemicals, Allentown, PA, March 14, 1980.

[†] Telephone communications with S.O. Akinbami, Union Carbide Corporation, Linde Division, Tonawanda, NY, November 1979.

TABLE 15. PERFORMANCE OF THE HIGH PURITY OXYGEN SYSTEM PILOT PLANTS

	Influent concentration, mg/ℓ				Percent removal				Reference
	BOD	COD	TSS	TOC	BOD	COD	TSS	TOC	
Petrochemical complex	885	1,905	85	-	97	75	-	-	7
Petrochemical complex	2,670-4,040	4,030-7,150	-	1,310-2,350	77-90	54-76	-	60-76	8
Pulp and paper mill	277-445	874-1,383	-	-	91-93	52-60	-	-	8
Kraft mill effluent	215-291	814-1,040	86-109	-	77-91	35-45	-	-	4
Municipal plus chemical industry, iron processing, and textile waste	348	767	114	-	95	77	68	-	9

TABLE 16. TYPICAL COAL CONVERSION WASTEWATER CHARACTERISTICS (7) (WASTEWATER DILUTED 1+19 WITH RIVER WATER PRIOR TO TREATMENT)

Constituent/parameter	mg/ℓ
BOD_5	30,000
COD	50,000
TOC	12,000
TC	13,000
Phenols	8,500
Acetone	150
Methyl ethyl ketone	100
Pyrrole	150
Pyridine	110
Cresols	2,800
Xylenols	1,300
Oil and grease	500
Ammonia, as N	4,600
TKN, as N	4,700
Nitrate, as N	200
Total sulfur, as S	3,000
pH	9.5 units

TABLE 17. DILUTED COAL CONVERSION WASTEWATER TREATMENT RESULTS WITH THE HIGH PURITY OXYGEN PROCESS (7)

Characteristic	Influent	Effluent	Percent removal
BOD_5, mg/ℓ	1,700	21	99
COD, mg/ℓ	2,800	177	94
TOC, mg/ℓ	690	33	95
TSS, mg/ℓ	140	64	55
Oils, mg/ℓ	30	10	70
Phenols, mg/ℓ	700	1.2	99+

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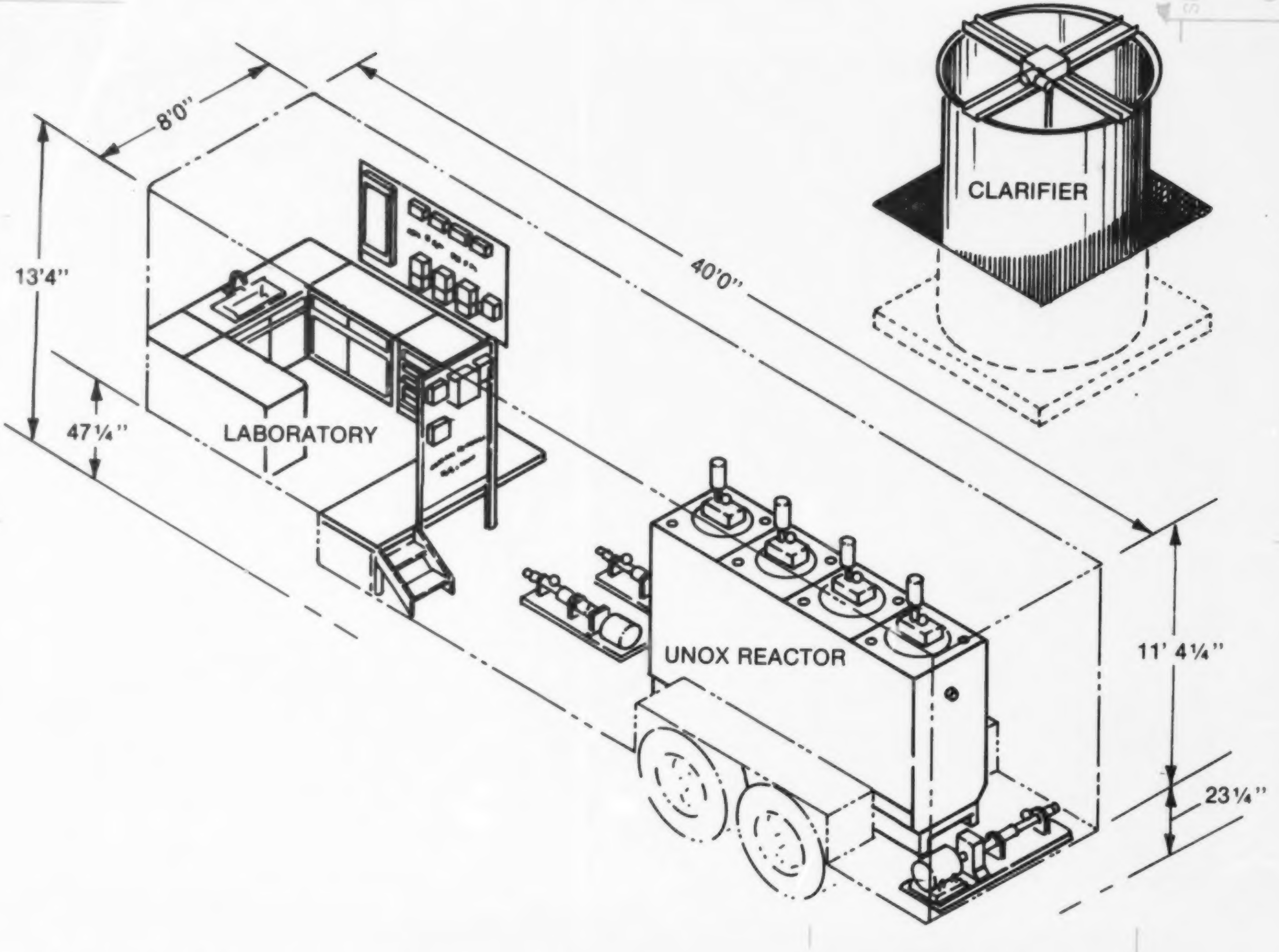
CLARIFIER
8'0"
40'0"
13'4"
47¼"
LABORATORY
UNOX REACTOR
11' 4¼"
23¼"

Figure 10. Schematic diagram of the UNOX Mobile Unit Pilot Plant and the external clarifier.*

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* Drawing provided by S.O. Akinbami, Union Carbide Corporation, Linde Division, Tonawanda, NY, October 23, 1979.

(1,600 gal) four-stage UNOX reactor. Each stage (1,512 ℓ or 400 gal in capacity) contains a submerged turbine rotating sparger device, which includes a mechanical mixer and a gas recirculation compressor. Rotameters are provided on each stage to monitor and control the recirculation flow. Influent, return sludge, and sludge wasting pumps are provided. These are variable speed, positive displacement Moyno pumps. Influent and return sludge can be fed to any of the four reactor stages. An in-line oxygen gas composition system is provided (Servomex analyzer), as is a hydrocarbon monitoring system (LEL meter). A dry gas meter is used to monitor the oxygen feed flow and a wet drum meter is used to monitor the vent gas flow. Portable pH, dissolved oxygen, and sludge blanket meters are provided to obtain daily operational data. The mobile unit also houses a laboratory for wastewater analysis and process control work.

The secondary clarifier associated with the UNOX pilot plant is 2.1 m (7 ft) in diameter and 3.35 m (11 ft) deep. This unit is externally mounted and requires a hole, approximately 1.5 m (5 ft) deep. In field applications, the trailer itself is positioned on a firm, flat surface, such as a roadway. Ideally, this would be adjacent to a non-paved area for clarifier installation.

When handling wastes containing volatile flammable organics, the buildup of volatile hydrocarbons in the oxygen rich space of the UNOX system could constitute a hazard. The system, however, does include features for the elimination of combustible gas buildup in the reactor. To eliminate ignition sources, no electrical components are installed under the tank cover and no metal-to-metal contact of moving parts is present. To eliminate the collection of combustible vapors, combustible gas analyzers are employed to continuously monitor for the presence of combustible materials. Should an approach to a lower explosive limit (LEL) occur, the analyzer activates the necessary controls that cause the gas space to be purged with air until the gas and liquid have carried the combustible material out of the system.

Union Carbide Corporation, which markets the UNOX process, offers a total pilot plant program for the evaluation of the applicability of the UNOX process to the treatment of specific wastewater and for the development of criteria for the design of full-scale units. The program includes the pilot plant equipment described above (that is, van and clarifier), a full-time on-site technician (40 hour work week and 24 hour on-call) and the services of a pilot plant engineer who directs the program from Tonawanda (NY) and makes periodic site visits. The oxygen required in these programs is also provided by Union Carbide. The customer is expected to provide installation (teardown) labor, operating manpower, analytical support, and utilities. A typical installation requires three to four days each for an electrician and a pipefitter or millwright. A "cherry picker" or small crane is also required for the clarifier installation. The operating manpower consists of 24-hour coverage to take samples and routine measurements. The utilities include 240-volt, single-phase, 200-amp electrical service* and a supply of potable water (for example, a garden hose supply is adequate).

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*Although the existing UNOX pilot plant requires an external power supply source, there is sufficient room on the van for installation of a diesel electric power generator.

The mobile UNOX system can be either rented or purchased from the Union Carbide Corporation. The estimated rental costs are as follows*:

(a) $5,000 for the checkout and refurbishment of equipment to make it operational

(b) $420/day for on-site service including engineering consultation on program plan and execution

(c) $70/day rental of equipment

(d) transportation charges to get the equipment from Tonawanda to the site of operation and back again to Tonawanda

The purchase price for the UNOX mobile unit is between $200,000 and $250,000.

USE OF HIGH PURITY OXYGEN ACTIVATED SLUDGE PROCESS IN MOBILE UNITS FOR TREATMENT OF WASTE SPILLS

This section evaluates the feasibility of using a high purity oxygen activated sludge process in a mobile unit to treat concentrated waste spills.

Pertinent Features of High Purity Oxygen Activated Sludge Process for Use in Mobile Units

Although high purity activated sludge process is commercially available in mobile field units, being a biological process it suffers from a number of limitations that may restrict its applicability or make extensive wastewater pretreatment necessary. These limitations primarily relate to the requirement for very long aeration time (and hence large reactor size) for treating concentrated wastes, inapplicability to wastes containing very high concentrations of toxic substances or refractory organics, and the considerable time required for process startup and waste acclimation. Since many chemical spill incidents involve toxic or refractory chemicals and highly concentrated wastes, the use of activated sludge process may not be applicable to many such situations. Relatively dilute wastes (200-500 mg/ℓ BOD_5) that do not contain concentrations of toxic substances, however, can be treated by high purity oxygen activated sludge process in mobile units such as those that are currently available commercially.

Another shortcoming of the biological processes that may limit their application to short-term emergency response situations is the often lengthy start-up time required and the requirement for elaborate and lengthy bench-scale or small pilot plant scale testing to determine waste treatability and optimum treatment conditions. Generally, it takes several weeks for activated sludge systems to stabilize. This time period will vary depending on the type of waste being treated. Start-up times can be decreased if the wastewater is "seeded" with an optimal mix of microorganisms. With a mobile unit that treats wastewaters of highly variable types, it may be extremely difficult to maintain the variety of cultures needed to seed a specific wastewater.

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*The costs shown are 1979 estimates and do not include taxes and any performance bonds.

As a biological process, high purity oxygen activated sludge process is susceptible to "shock" loads because of fluctuations in the characteristics of the raw wastewater. If such fluctuations are anticipated in field applications, use of an equalization basin would be necessary to "smooth" variations in the quality of feed to the mobile unit.

High purity oxygen activated sludge process would not be suitable for treatment of wastewaters containing high concentration of volatile hydrocarbons and other organics (for example, when spills of ether, benzene, pentane, etc., are involved). The presence of such low flash-point compounds can present a potential fire hazard and, as noted earlier, the UNOX system is equipped with hydrocarbon analyzers and control systems that deactivate the system when dangerously high concentrations of volatile hydrocarbons are detected in the oxygen-rich space of the reactor.

The operation of a mobile high purity activated sludge unit would require trained operators. As with most other processes considered, the process generates a residue (waste sludge) that may require further processing and disposal. The quantity of sludge varies with the type of wastewater and system design. For application to municipal sewage, about 0.35-0.45 kg of sludge (VSS) is produced per kg of BOD_5 removed. In field application, the waste sludge may have to be collected and transported to hazardous waste management facilities for disposal. As noted previously, oxygen for the process can be provided from a liquid oxygen source that would be delivered to this site in special containers*. The oxygen requirement varies with the process design and organic loading and would typically be in the 0.6 to 1.5 kg/kg of BOD_5 removed (10). Most waste spills would be deficient in nutrients (for example, nitrogen and phosphorus compounds) or have a pH too high or too low for effective biooxidation. Such wastewaters would require addition of supplementary nutrients or acids or alkali for pH adjustment.

Engineering Evaluation and Cost Estimates

The largest existing high purity activated sludge process mobile unit has a reactor capacity of 6,000 ℓ (1,600 gal). When handling municipal wastewaters or dilute industrial wastewaters, the system can be operated with a detention time of as low as one hour. At one-hour detention time, the system would have a hydraulic capacity of 144,000 ℓ/day (38,400 gpd). For treating higher concentration wastewaters, a significantly higher detention time would be required that would subsequently reduce the hydraulic capacity of the unit. At a 24-hour detention time, which is commonly required for the treatment of industrial wastes having BOD_5 concentrations in the 1,000-3,000 ppm range, a unit with a reactor size of 6,000 ℓ (1,600 gal) can handle a flow of only 6,000 ℓ/day (1,600 gpd). The hydraulic capacity of the system would be reduced even further when higher detention times are required. It is estimated that the largest reactor size that can be accommodated on a single trailer is 47,300 ℓ (12,500 gal); at a detention time of 48 hours, this reactor would have a hydraulic capacity of only 23,650 ℓ/day (6,250 gpd) that would be too small for mobile unit application to the management of large spills.

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*Large quantities of liquid oxygen can be delivered with only a few hours notice to virtually any place in the Continental United States. This capability currently provides oxygen supply backup to thousands of steel manufacturers, metal fabricators, hospitals, and chemical users throughout the United States.

The existing UNOX mobile units require an external power source. These units, however, can also carry a generator for on-board power generation. The overall power required for liquid mixing and gas recirculation will vary with specific system configuration, but will generally lie between 0.02 and 0.03 kw per 1,000 ℓ (0.08 and 0.14 HP per 1,000 gal) of mixed liquor under aeration. For a 46,300 ℓ (12,500 gal) reactor capacity, the power requirement would be in the 0.74 to 1.3 kw range that can be provided with a 5 kw diesel engine.

As discussed previously, the oxygen required in the process can be purchased in liquid form and would generally be delivered to the site by the suppliers. Typically, between 0.6 and 1.5 kg of oxygen would be required per kg of BOD_5 removed. Liquid oxygen is delivered in bulk or in tanks. The price varies considerably; one supplier on the west coast quotes unit purchase prices for bulk and tank load liquid oxygen of $42/metric ton ($38/ton) and $57/metric ton ($52/ton), respectively. The requirements for other chemicals (nutrients and pH adjustment chemicals) would be dependent on the wastewater characteristics and would generally be very small (typically, a BOD:N:P ratio of 100:5:1 would be required for optimum biooxidation).

Typical rental and purchase costs and operating labor requirements for the existing UNOX mobile units were presented earlier.

REFERENCES

1. Union Carbide UNOX System Wastewater Treatment, Union Carbide Corporation, Linde Division, Bulletin F-3424.

2. Albertsson, J.G., et al. Batavia I, EPA-PNI 17050 DN W, May 1970.

3. Chapman, T.D., et al. Effect of High Dissolved Oxygen Concentration in Activated Sludge Systems, Journal of Water Pollution Control Federation Vol. 48, No. 11, pp. 2486-2510, Nov. 1976.

4. Peterson, R.R. Design Criteria for High Purity Oxygen Treatment of Kraft Mill Effluent, Journal of Water Pollution Control Federation Vol. 47, No. 9, pp. 2317-2329, Sept. 1975.

5. Bell, B.A. and J.M. Welday. Comparison of Completely Mixed Activated Sludge and UNOX Treatment of Brewery Wastes, in Water-1977, AIChE Symposium Series, No. 178, Vol. 4, pp. 29-36, 1978.

6. Nash, N., et al. Oxygen Aeration at Newton Creek, Journal of Water Pollution Control Federation 49(3), pp. 388-400, March 1977.

7. Hardisty, D.M. and H.E. Bishop, Jr. Wastewater Treatment Experience at Organic Chemical Plants Using a Pure Oxygen System, in Water-1976: II. Biological Wastewater Treatment, AIChE Symposium Series, No. 167, Vol. 73, pp. 140-144, 1977.

8. Matsch, L.C. and W.C. Dedeke. Use of Pure Oxygen in the Secondary Treatment of Wastewater, The Petroleum/Petrochemical Industry and the Ecological Challenge, AIChE Symposium Series, No. 135, Vol. 69, pp. 175-178, 1973.

9. Vaseleski, R.C. The UNOX Process: Effective Wastewater Treatment Practice, in Water-1977, AIChE Symposium Series, No. 178, Vol. 4, pp. 23-28, 1978.

10. EPA Technology Transfer Seminar Publication, Oxygen Activated Sludge Wastewater Treatment Systems - Design Criteria and Operating Experience, August 1973.

SECTION 9

COMBINED OZONATION AND ULTRAVIOLET RADIATION

PROCESS DESCRIPTION

Process Principle

Ozonation in combination with ultraviolet radiation (O_3/UV) is a newly-developed chemical oxidation process that has proved effective for the destruction of many organic compounds including refractory chemicals and organometallic complexes, and reduced inorganic substances in aqueous systems. The oxidation takes place in a reactor where the waste is contacted with ozone and UV radiation simultaneously. The use of ultraviolet radiation enhances the oxidation power of ozones thereby increasing the reaction rate and oxidation efficiency.

By itself, ozone is a very strong oxidizing agent with an oxidation power higher than those of chemicals such as chlorine compounds, hydrogen peroxide, and potassium permanganate which are commonly used for water disinfection and oxidative treatment of waters and wastewaters. Ozone is extensively used in Europe for water disinfection, for the treatment of waters containing iron and manganese, and as a pretreatment method to convert toxic and refractory substances in a wastewater into biodegradable materials. Ozone exists as a gas at ordinary temperatures and pressures (boiling point of ozone is - 112°C at atmospheric pressure)(1). It is only slightly soluble in water (about 20 times as soluble as oxygen). Because of its low solubility, supplying ozone at a sufficiently fast rate to the reactor becomes a major mass transfer problem in the treatment of concentrated wastes (1), especially those containing substances that are rapidly oxidizable with ozone (for example, sulfides, nitrites, bacteria, phenols, and unsaturated organics). Ozone transfer to the wastewater, however, would not be a major problem for substances that are oxidized very slowly with ozone (for example, acetic acid, oxalic acid, urea, and unsaturated aliphatic alcohols).

In actual application where ozone is used alone, complex organic substances are only partially oxidized. These substances are generally converted to intermediate products such as acetic and oxalic acids and to other products that are either refractory to ozone oxidation or that undergo oxidation at such a low rate that they are not removed from the system during the treatment period. The effectiveness of ozone for wastewater treatment, however, can be enhanced by simultaneous application of ultraviolet radiation. Figure 11 is a comparison of O_3/UV combination treatment with the application of ozone

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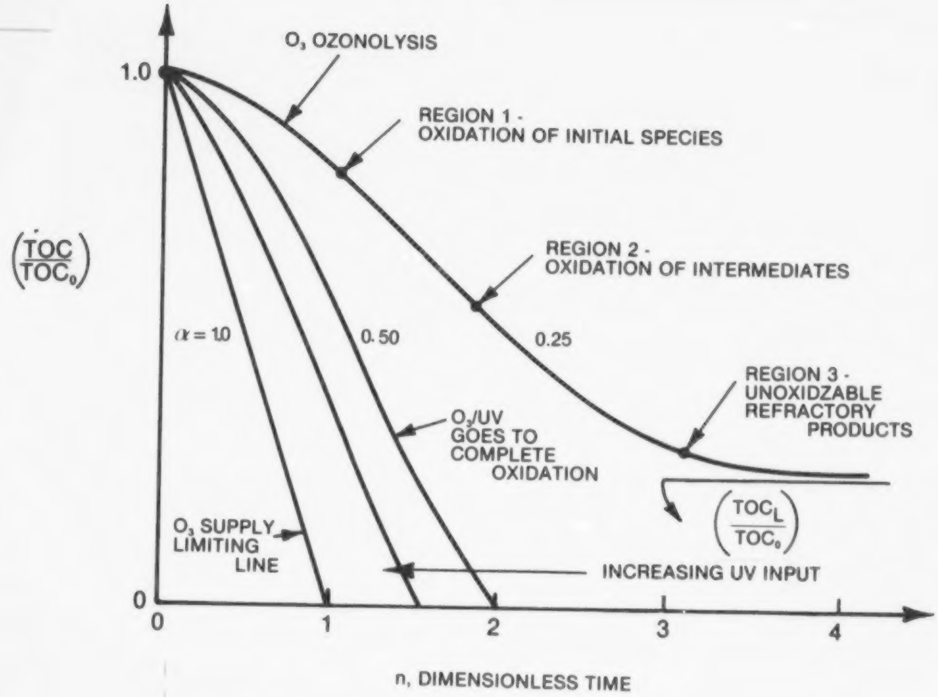

Figure 11. Comparison of O_3/UV combination treatment with ozonation (2) (α = fraction of ozone used by the reaction).

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alone. The figure indicates that O_3/UV is superior to ozonation both in terms of rates and efficiency of TOC removed.

While the specific role of the ultraviolet radiation in enhancing the efficiency of ozonation is still under investigation, it is currently hypothetized that the major effect of radiation is to bring about a photodecomposition of the substances undergoing oxidation, thereby converting them to more reactive "free radical" species.

Table 18 is a list of organic compounds that have been determined to be economically treated by O_3/UV process. The substances listed range from simple polar aliphatic compounds such as acetaldehyde and acetic acid (which cannot generally be removed from wastewaters by carbon adsorption) to highly nonbiodegradable complex and toxic compounds such as PCB and kepone. Although not listed in the table, metal complexes of cyanides that cannot be oxidized with chlorine or ozone alone are completely destroyed by O_3/UV treatment (2).

Process Flow Diagram and Other Considerations in O_3/UV Treatment

Figure 12 presents one commercial design for a O_3/UV reactor for wastewater treatment*. Since the optimizations of the O_3/UV contacts with the wastewater and the O_3 mass transfer are important design parameters, the reactor is divided into compartments (created by use of baffels) with cylindrical UV lights (similar to commercial fluorescent lights) placed vertically at equal distances along the flow path in each compartment. Ozone, which is generated on-site, is introduced as a gas into the reactor through diffusers that are located at the bottom of each compartment. The excess ozone in the reactor offgas is discharged to the atmosphere. In general, the specifics of a reactor design such as reactor size, number of compartments, and spacing of ozone diffusers and UV lights are determined by the characteristics of the wastewater to be treated and the desired process efficiency. For most applications, the optimum design can best be determined using pilot plant tests.

Wastewater characteristics which would impact process efficiency and hence reactor design are wastewater flow, nature and concentration of substances to be oxidized and concentration of suspended solids which would interfere with the passage of UV light through the wastewater, and wastewater temperature. Even though the reaction rate increases with the rise in temperature, increased temperature can reduce the overall efficiency by reducing the half-life of ozone and its solubility in wastewater. Although pH of the wastewater is not considered a critical factor in determining process efficiency, for certain wastes (for example, cyanides) maintenance of a specific pH level is necessary to avoid generation of toxic gases (for example, hydrogen cyanide). Pilot plant studies should be conducted to determine the optimum reactor design and operating conditions for specific wastes.

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*Another commercial design, the "multi-stage reactor", uses several reactors in series instead of one reactor with multiple compartments. Each reactor "Stage" is a "completely" mixed system with the mixing provided by a centrally-located mechanical mixer.

TABLE 18. LIST OF ORGANICS DETERMINED TO BE ECONOMICALLY TREATABLE BY THE O_3/UV PROCESS (4)

Acetaldehyde
Acetic acid
Alcohols
Aldrin
Amines
Anisole
Benzoic acid
Chelating compounds
Chlorinated phenols
Chlorobenzene
Detergents
Dieldrin
Dioctylpthalate
Endrin
Ethylene dichloride
Formaldehyde
Formic acid
Glycerols
Glycine
Glycols
Hydroquinone
Kepone
Methylene chloride
Nitrobenzene
Nitrophenol
Organic phosphates
Organosulfur compounds
Organo-tin compounds
PCB's
Phenol
Phthalic acid
RDX
Sodium acetate
Styrene
Sugars
TNT
Vinyl chloride
Xylenol

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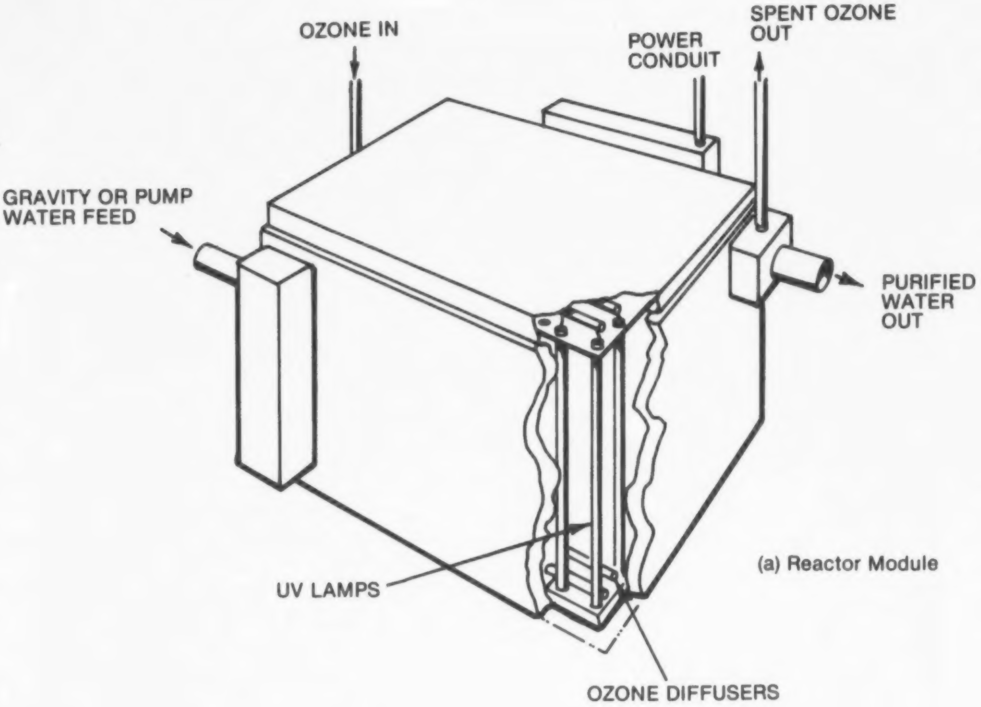
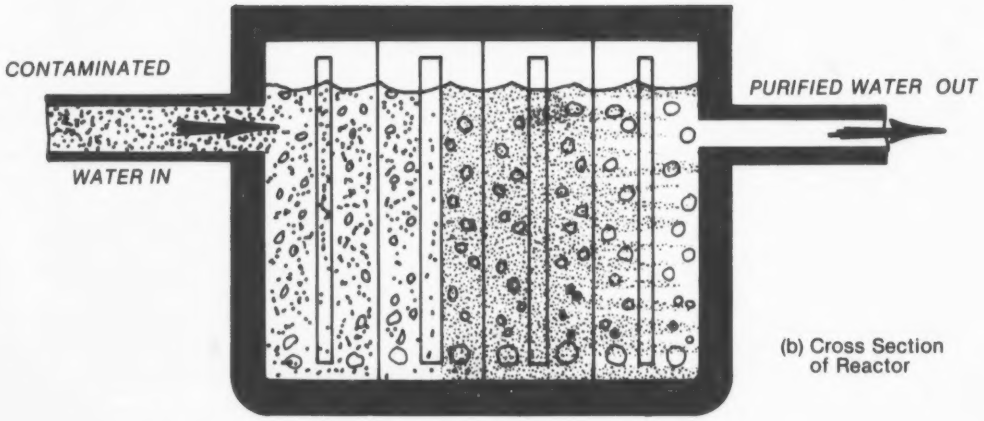

OZONE IN
POWER CONDUIT
SPENT OZONE OUT
GRAVITY OR PUMP WATER FEED
PURIFIED WATER OUT
UV LAMPS
OZONE DIFFUSERS

(a) Reactor Module


CONTAMINATED WATER IN
PURIFIED WATER OUT

(b) Cross Section of Reactor

Figure 12. Schematics of an O_3/UV reactor.

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PROCESS APPLICATIONS AND RELATED STUDIES

Commercial Scale Municipal/Industrial Applications

Because of the relatively new nature of the O_3/UV process, there are only a few full-scale plants currently in operation. These plants, for which little design and operating data have been published, reportedly handle cyanide and organic wastewaters from a tool company, photographic and metal plating waste from a U.S. Army ammunition plant, and a combination of organic nitrogen and cyanide waste from a company in France (2). There are also a number of plants in the various design phases including a plant to treat PCB from a capacitor production facility and "pink water" from a U.S. Army ammunition plant (4).

Pilot and Laboratory Scale Studies

A number of pilot plant studies have been conducted or are currently in progress to assess the applicability of O_3/UV to the treatment of various wastewaters including wastewaters from army field hospitals, a contaminated groundwater from an Army arsenal, "pink water" from an army ammunition plant, organic contaminated brine and elutriate containing PCB's, and wastewater from a paint-stripping operation (4). Typical results obtained in some of these applications are shown in Table 19.

A pilot plant was set up at General Electric Company's Capacitor Product Department facilities in Hudson Falls, New York, to demonstrate the efficiency and cost effectiveness of the O_3/UV system for destruction of PCB's (5 to 40 ppb) from an industrial effluent (5). Results of this study indicated that it is both feasible and economical to reduce PCB's to below one ppb. The capital costs for a 151,400 ℓ/day (40,000 gpd) and 567,800 ℓ/day (150,000 gpd) plant were estimated to be $124,500 and $300,000, respectively; the operating costs were estimated to be $1.15/1,000 ℓ ($4,35/1,000 gal) and $0.58/1,000 ℓ ($2.21/1,000 gal), respectively. In another study that compared the cost of O_3/UV and carbon adsorption to remove PCB's to one ppb level, it was found that O_3/UV is actually more economical than the carbon adsorption (see Table 20)(6).

Pilot studies have shown that for some wastewaters it is advantageous to use several reactors in stages instead of a single-stage or a single-compartment reactor (6). As discussed earlier, ozone mass transfer may be the rate limiting step for oxidizing certain chemicals. With staged reactors/compartments the ozone and UV dosages can be adjusted in each stage/compartment to the actual "demand" that varies as the treatment progresses. Table 21 shows the treatment results for a six-stage reactor treating a wastewater containing metal-complexed cyanides. The data show that ozone alone in the first few stages can reduce the complexed cyanide to very low levels, with the UV light used primarily as the "polishing" treatment in the last stages. Final concentration of less than 0.3 ppm of complexed Fe cyanide, and less than 0.1 ppm of Cu- or Ni-complexed cyanides can thus be obtained.

The effectiveness of O_3/UV and ozonation alone have been compared in a number of laboratory and pilot plant studies using a spectrum of wastewaters including secondary effluent, TNT and hospital wastes (4), and synthetic

TABLE 19. TYPICAL O_3/UV PILOT PLANT TEST RESULTS (3)

Wastewater	Influent analysis, mg/ℓ	Effluent analysis, mg/ℓ	Residence time, min	O_3 mass flow, mg/min	No. of 40w UV lamps
Pink water	70 TOC 76 TNT	5 TOC 1 TNT	177	721	29
Ground water	2.6 DIMP*	0.012 DIMP	95	400	29
Dredge spoil elutriate	2.6 TOC 0.030 PCB's	2.0 TOC <0.00> PCB's	83	410	18

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*Disporopylmethyl phosphonate.

TABLE 20. COMPARISON OF THE ECONOMICS OF O_3/UV AND CARBON ADSORPTION FOR THE TREATMENT OF PCB WASTEWATERS (6)

	Flow (gpm)		
Capital cost ($1,000)	20	160	1,700
O_3/UV	152	422	1,380
Carbon adsorption	174	570	3,407
Operating cost ($/1,000 gal) Including amortization			
O_3/UV	3.49	1.72	1.09
Carbon adsorption	4.17	1.73	1.11

TABLE 21. OXIDATION OF METAL COMPLEXED CYANIDE IN A STAGED REACTOR (6)

	Influent	Effluent from reactor stage					
		1	2	3	4	5	6
Cu-complexed							
CN, mg/ℓ	4,000	17	0.5	<0.1			
Cyanate, mg/ℓ	0	-	-	110			
Temp., °C	20	20	20	66			
pH	11.5	-	-	7.7			
UV watts/ℓ	-	0	0	1.2			
Ni-complexed							
CN, mg/ℓ	4,000	110	0.6	<0.1			
Cyanate, mg/ℓ	0	-	-	470			
Temp., °C	20	20	20	66			
pH	11.8	-	-	8.5			
UV watts/ℓ	-	0	0	1.2			
Fe-complexed							
CN, mg/ℓ	4,000	2,680	1,630	710	105	13	<0.3
Cyanate, mg/ℓ	0	-	-	-	-	-	47
Temp., °C	20	66	66	66	66	66	66
pH	-	-	-	-	-	-	8.9
UV watts/ℓ	-	0	0	0	0	0	1.2

wastewaters using model chemicals such as pentachlorophenol, malathion, and iron-organic complexes (6). The results from these studies provide the basis for the generalized plot in Figure 11. When used for disinfection, O_3/UV has been shown to require only 10 percent as much ozone as ozonation for achieving the same degree of disinfection (6).

Mobile Unit Applications

At the present time, there is no report as to the existence of any O_3/UV mobile treatment units.

USE OF O_3/UV IN MOBILE UNITS FOR TREATMENT OF WASTE SPILLS

Pertinent Features of O_3/UV Treatment for Use in Mobile Units

Based on discussions with the process developers, nearly all the requirements for the applicability of a process to the treatment of waste spills in a mobile unit would be met by the O_3/UV process. The O_3/UV reactors are modular, portable, and commercially available. The system can be started and shut down relatively quickly, can be serviced conveniently, would not require skilled labor for field operation, and can be operated with the electric power produced on-site by a diesel generator. The system can handle troublesome wastes (such as cyanide) and convert them to harmless end products (such as water and CO_2). The major shortcomings of the O_3/UV unit relate to the limited amount of ozone that can be generated on-site and the discharge of residual ozone to the atmosphere. The amount of ozone that can be generated on-site in a mobile unit may be less than the quantity required in an application. O_3/UV is a process that has been commercialized only recently, and little operating and design data are available for the process. O_3/UV process is currently being offered by the following two companies: Houston Research, Inc., Houston, Texas and Westgate Research Corp., West Los Angeles, California. Houston Research offers a "multi-stage" reactor design, whereas Westgate Research offers a single-stage, multiple-compartment design. Both designs offer units that are modular, portable, and can be skid mounted. The modular design allows flexibility that the treatment capacity can be altered via use of additional modules, number and combination of UV lamps, or adjustments of ozone flow to each stage. The O_3/UV units require minimal labor for operation and maintenance. The process start-up merely involves turning on the wastewater pump, the UV lights, and the ozone-generator. Periodic cleaning of the reactor by opening the drain valves at the bottom may be required to prevent excessive build-up of sludge at the bottom of the reactor. The "burned" or "weak" UV lamps would require replacement. On the average a UV lamp would have a life expectancy of about one year.

The O_3/UV process is especially suitable for handling hard-to-treat wastes (for example, complexed cyanides and refractory organics). When treating these wastewaters, the end products of O_3/UV treatment are primarily harmless gases. The power for the operation of an O_3/UV unit can be supplied by a diesel electric generator that can be housed in the same or a separate mobile unit.

Some of the major shortcomings of the O_3/UV process for mobile unit application relate to the heavy weight and large size of the ozone generator and the discharge of residual ozone to the atmosphere. The largest ozone generator that can be installed on a trailer would generate 91 kg O_3/day (200 lb/day)*. As discussed before, theoretically, eight parts of ozone is required to remove one part of TOC in wastewater. Thus a 91 kg/day O_3 generator can theoretically handle a wastewater containing 11.3 kg/day of TOC. For spills containing 10 ppm and 1,000 ppm TOC, the theoretical amounts of wastewater that can be treated by the unit would be 1.13 x 10^6 ℓ/day (3 x 10^5 gpd) and 1.13 x 10^4 ℓ/day (3 x 10^3 gpd), respectively. For large volume, concentrated waste spills, the O_3/UV can be used as a polishing step after bulk of the organics are removed by other treatment methods (for example, carbon adsorption).

Although the commercial designs feature the use of a catalytic convertor for destruction of unused ozone in the reactor off-gas, the destruction efficiency is usually less than 100 percent and some residual ozone (about 5 percent of the ozone fed to the wastewater) would escape to the atmosphere. Good ventilation is required for safety of the operating personnel. The maximum ozone exposure levels proposed by various regulatory and professional organizations are listed in Table 22.

Engineering Evaluation and Cost Estimates

Based on data obtained from one O_3/UV process developer, a preliminary design has been developed for a 227,000 ℓ/day (60,000 gpd) O_3/UV single-stage multiple-compartment unit for use on a trailer flatbed. The unit would be constructed of stainless steel, sized for one hour detention time, and would have dimensions of 3.7 m long, 2.1 m wide, and 1.6 m high (21 ft x 7 ft x 5 ft). The UV light would be supplied by 336 40w UV lamps and the ozone by a 91 kg/d (200 lb/d) generator that uses compressed air from an air compressor. The entire system, including wastewater pump, air compressor, ozone generator, reactor, and catalytic convertor would weigh about 9,070 kg (20,000 lb). Power can be supplied by a 125 kw diesel generator. The power requirements for the operation of the UV light and the ozone generator are estimated at 22 kw and 83 kw, respectively. The diesel generator would have the approximate dimensions of 2.5 m (l) x 0.9 m (w) x 1.3 m (h) or 8.3 ft x 2.8 ft x 4.3 ft and would weight about 2,270 kg (1,000 lb).

The major logistics support required in field application relates to possible requirements for UV lamp replacement. Under normal operation, it is unlikely that lamp replacement would be required in the field during short-term operations. Based on experience with pilot plant operation, a UV lamp life of one year is estimated for continuous operation.

The estimated total capital cost for the O_3/UV unit and the diesel electric generator are $265,000 and $20,000*, respectively. These costs include

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*Information supplied by Jack D. Zeff, Westgate Research Corporation, West Los Angeles, CA, in a meeting on February 23, 1979.

TABLE 22. OZONE EXPOSURE LEVELS PROPOSED BY VARIOUS REGULATORY AND PROFESSIONAL ORGANIZATIONS

Agency/organization	Exposure level
Occupational Safety and Health Administration (OSHA)	Maximum permissible exposure to airborne concentrations of ozone not in excess of 0.1 mg/ℓ (by volume) averaged over an 8-hour work shift
American National Standards Institute/American Society for Testing and Materials (ANSI/ASTM)	Control occupational exposure such that workers will not be exposed to ozone concentrations in excess of a time weighted average of 0.1 mg/ℓ (by volume) for eight hours or more per workday, and that no worker be exposed to a ceiling concentration of ozone in excess of 0.3 mg/ℓ (by volume) for more than ten minutes
American Conference of Government Industrial Hygienists (ACGIH)	Maximum ozone level of 0.1 mg/ℓ (by volume) for a normal 8-hour work day or 40-hour work week, and a maximum concentration of 0.3 mg/ℓ (by volume) for exposure of up to 15 minutes.
American Industrial Hygiene Association	Maximum concentration for 8-hour exposure of 0.1 mg/ℓ (by volume)

the equipment costs (air compressor, ozone generator, reactor with UV lamps, catalytic converter, wastewater pump, piping, and valves) and the engineering and installation fees.

The major operating and maintenance cost elements for the O_3/UV unit are electrical power for ozone generating and operation and replacement of UV lamps. For field applications, the operating cost per unit volume of wastewater treated would vary depending on the specific characteristics of a spill situation (for example, waste characteristics, waste volume, location of spill, etc.). Assuming that in most field applications the mobile unit will have to be powered by a diesel electric generator, the fuel for the generator would constitute one of the major items of operating expense. A 125 kw diesel generator would consume about 76 ℓ/hr (10 gal/hr) of fuel ($6/hr).

REFERENCES

1. Miller, G.W., R.G. Rice, et al. An Assessment of Ozone and Chlorine Dioxide Technologies for Treatment of Municipal Water Supplies, EPA-600/2-78-147.

2. Prengle, H.W., Jr. Recent Experience - O_3/UV Photo-Oxidation of Industrial Wastewater and Source Water Components, presented at IOI Ozone Symposium and Exposition, Los Angeles, California. May 23-25, 1978.

3. Leitis, E. An Investigation into the Chemistry of UV-Ozone Purification Process, annual report on research supported by NSF under Grant Number ENV 76-24652, 1979.

4. Zeff, J.D. Ultrox Process Treatment of Organic Wastewater, presented at the 3rd Annual Conference on Treatment and Disposal of Industrial Wastewaters and Residues, Houston, Texas. April 18-20, 1978.

5. Arisman, R.K., T.C. Crase, et al. Destruction of PCB's in Industrial and Sanitary Waste Effluents by the Ultrox^R (UV-Ozone) Process, presented at the AIChE 86th National Meeting, Houston, Texas. April 1-5, 1979.

6. Prengle, H.W., Jr. and C.E. Mauk. New Technology: Ozone/UV Chemical Oxidation Wastewater Process for Metal Complexes, Organic Species and Disinfection, Water-1977, AIChE Symposium Series 178, Vol. 76, p. 228, 1978.

SECTION 10

CHEMICAL TREATMENT
(Precipitation/Coagulation)

PROCESS DESCRIPTION

Process Principle

Removal of substances from aqueous systems by addition of chemicals that form insoluble precipitates with such substances is widely used for the treatment of municipal and industrial waters and wastewaters. Examples of such applications include hydroxide and carbonate precipitation of Ca^{++} and Mg^{++} (water softening), sulfide and hydroxide precipitation of Zn^{++}, Cd^{++}, Ni^{++}, Pb^{++}, etc., and Ca(II), Al(III), and Fe(III) precipitation of phosphates. Concentrations of cations and anions in aqueous systems are governed by the "solubility product constant" (Ksp) for the insoluble precipitate. For example, the solubility of Cu^{++} in water is governed by Ksp for $Cu(OH)_2$ (or Ksp for CuS when sulfide is also present):

$$Cu(OH)_2 \rightleftarrows Cu^{++} + 2OH^-$$

$$Ksp = [Cu^{++}][OH^-]^2 = 10^{-19} \text{ at } 20°C$$

$$[Cu^{++}] = \frac{10^{-19}}{[OH^-]^2}$$

where [] denote concentrations in mole/ℓ.

At a pH of 5.0 ($[OH^-] = 10^{-9}$ mole/ℓ), Cu^{++} concentration in water cannot theoretically exceed 0.1 mole/ℓ or 6,500 ppm. By increasing the pH to 9 (through addition of sodium hydroxide or lime), the solubility of Cu^{++} would reduce to 10^{-9} mole/ℓ or 0.065 ppb. Thus, near complete removal of Cu^{++} from solution should be achieved by hydroxide precipitation.

Most metal-hydroxide precipitation systems have amphoteric properties in that they are capable of exhibiting either acidic or basic characteristics depending on the pH level. In these systems, the metal cation becomes "resolubalized" as the pH is raised beyond the level of minimum solubility. As depicted in Figure 13, the pH of minimum solubility for Cu^{++} is close to 9. As the pH is raised beyond this level, the concentration of Cu^{++} in solution increases because of the formation of anionic complexes such as $Cu(OH)^-_3$. Figure 13 also indicates that the sulfides of the cations shown are considera-

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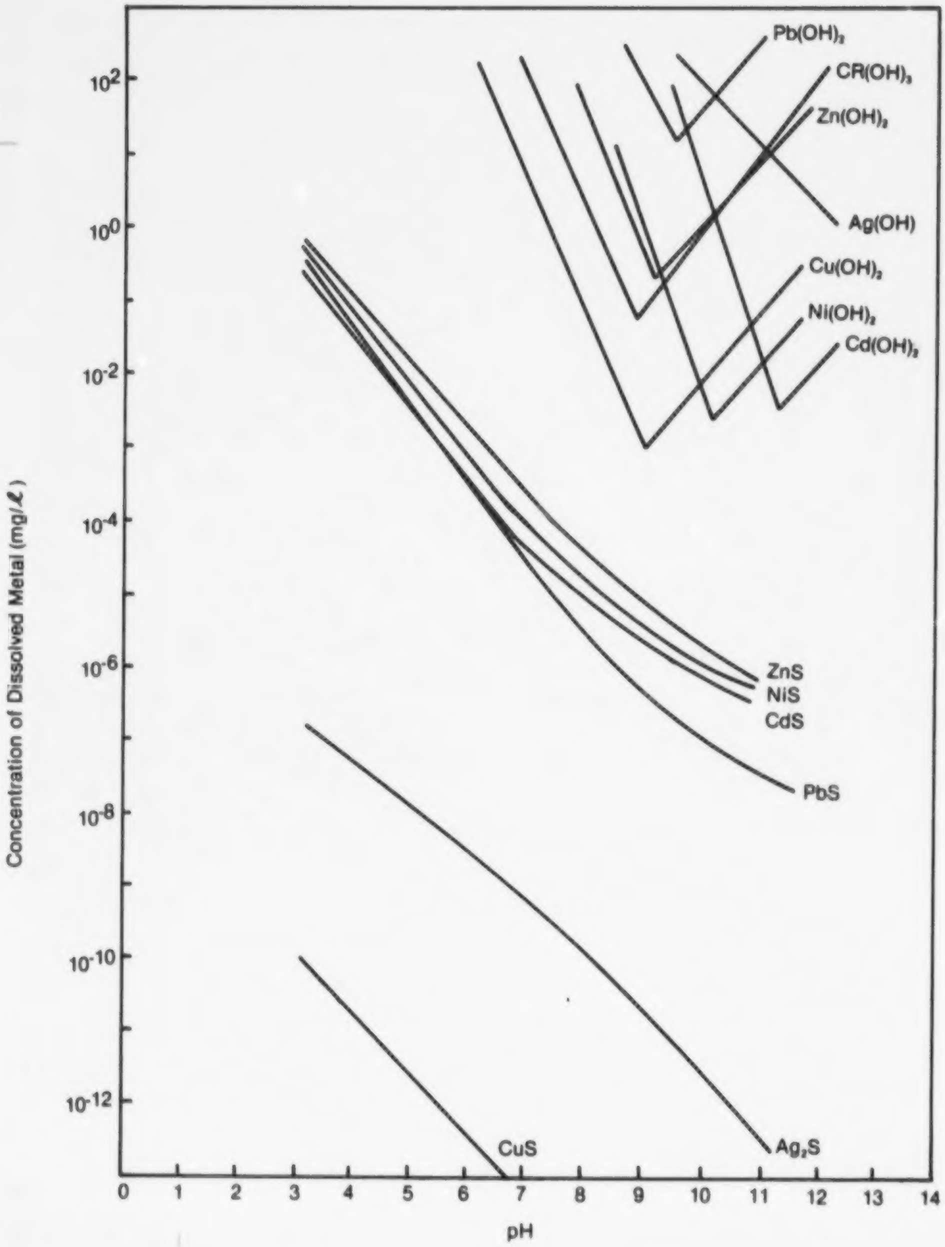

Figure 13. Solubility of metal hydroxides and sulfides.

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bly more insoluble than their hydroxides and hence more complete precipitation of the cations can be achieved at lower pH levels via addition of sulfide ion.

Hydrolyzing cations such as Al(III) and Fe(III) have been widely used in water and wastewater treatment for the removal of colloidal organic and inorganic particles. Although the exact mechanism of removal (coagulation) is not completely understood (despite extensive research), two theories have been forwarded to explain the observed phenomenon. The physical theory considers colloidal particles to be negatively charged and the coagulation to result from neutralization of the charge with the positively charged coagulant ions (Fe^{+++} and Al^{+++}) and their hydroxide complexes (for example, $Al(OH)^{++}$, $Fe(OH)^{+}_{2}$, etc.). The chemical theory considers coagulation to result from specific chemical reactions between the coagulant ions and their hydroxide complexes and the surface groups on the colloidal particles. In most coagulation systems a combination of both charge neutralization and chemical reactions is probably operative.

Determination of the Optimum Conditions for Precipitation and Coagulation

Solubility considerations such as those illustrated in the above example for the precipitation of Cu^{++} coupled with chemical analysis information on wastewater constituents can provide a reasonably accurate basis for defining the optimum conditions and chemical dosage requirements for precipitation of metal ions by addition of appropriate anions (for example, hydroxide, sulfide, carbonate or phosphate). Practical applications emphasize identification of operating conditions that are most conducive to the formation of readily settleable and/or filterable precipitates.

Many factors affect efficiency of coagulation/precipitation with Al(III) and Fe(III) salts. These factors, which include coagulant dose, pH, temperature, and ionic composition of the water, determine the nature and charge of the coagulant species and colloidal particles and anionic species that participate in the coagulation or precipitation reactions. Because of the extremely complex aqueous chemistry of Al(III) and Fe(III) salts and the coagulation/precipitation reactions, it is not possible to estimate the optimum conditions for coagulation/precipitation based on raw water analysis data. In practice the optimum conditions (pH and chemical dosage) are usually determined by a "trial-and-error" approach using the conventional "jar test".

The optimum pH of coagulation for the removal of turbidity from most natural waters is between 6 and 8 for Al(III) and Fe(III) salts. Removal of natural coloring matter and phosphates from waters and wastewaters can best be accomplished at a pH near 5 for Al(III) and close to 4 for Fe(III). For some systems such as polyphosphates, the pH range for optimum removal is extremely narrow with both Al(III) and Fe(III) salts (see Figure 14), and unless the pH is maintained within this narrow pH range (something which is impractical in actual water and wastewater treatment application), little removal can be expected. In the case of phosphates (ortho- and polyphosphates) it has been demonstrated that the decrease in the removal efficiency in the vicinity of the pH range for optimum removal and at coagulant doses exceeding the optimum dosage is because of the dispersion of the colloidal precipitates.

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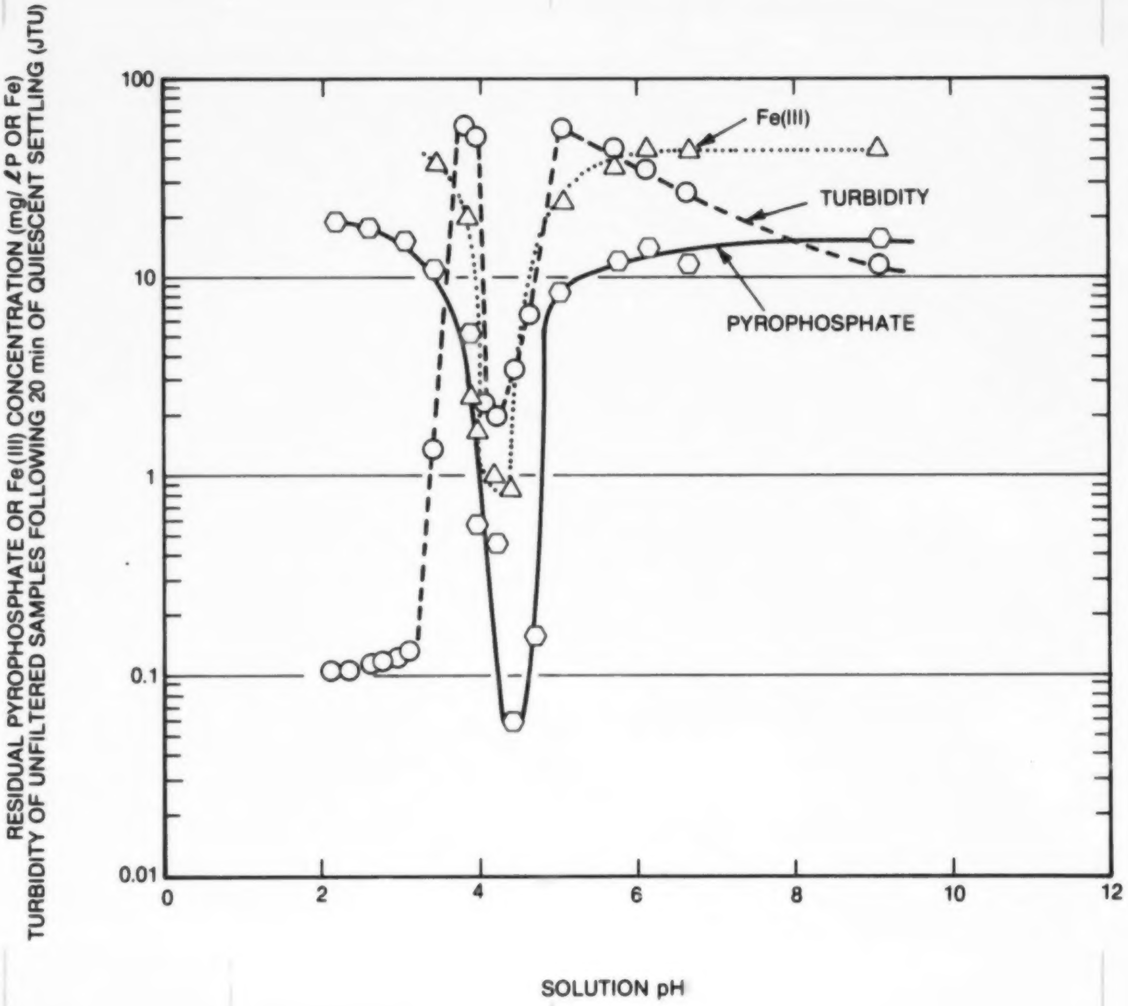

Figure 14. Precipitation of pyrophosphate with Fe(III) at a 2:1 cation-to-pyrophosphate equivalence ratio (1) (Initial pyrophosphate concentration, 18 mg/ℓP).

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As shown in Figures 15 and 16, the optimum pH and dosage range for orthophosphate removal can be extended when the water is passed through very fine filters subsequent to chemical reaction. In actual water and wastewater treatment application, the removal of coagulated or precipitated products in any subsequent settling and/or filtration step is improved by addition of coagulant aids such as organic polyelectrolytes to the water following addition of the coagulant salt.

Process Configuration and Considerations

Figure 17 is a flow diagram for the precipitation/coagulation and flocculation system. For industrial wastewaters that fluctuate in characteristics the raw wastewaters are fed to a retention/equalization basin where they are mixed to produce more constant feedwater quantity and quality. The equalized wastewater is pumped to the coagulation-flocculation unit that usually consists of three chambers: a mixing chamber, a flocculation compartment, and a sedimentation chamber. In the mixing chamber, the wastewater is flash-mixed with chemical coagulant*, coagulant aids and pH adjustment chemicals by means of vertical or horizontal mechanical paddles. The wastewater passes from the mixing chamber to the flocculation compartment where it is agitated by slowly moving paddles. It then flows into the sedimentation chamber by means of an inlet device that distributes the waste uniformly throughout the cross-sectional area of the chamber. Clarified water leaves the sedimentation chamber over a weir and is usually filtered prior to discharge/use. Residual sludge is scraped from the bottom of the sedimentation chamber and discharged.

Two basic types of systems are in commercial use: the sludge-blanket (reactor/clarifier) unit that combines mixing, flocculation, and settling in a single unit and the conventional system using a rapid mix tank, followed by a flocculation tank containing longitudinal paddles that provide slow mixing, and a conventional settling tank.

The sludges produced with Al(III) and Fe(III) salts in the treatment of certain industrial wastewaters (for example, pulp mill effluent which contains a high concentration of organics) are usually very bulky, voluminous, and difficult to dewater for ultimate disposal. Accordingly, coagulation with these hydrolyzing coagulants has not been employed in full-scale units for the treatment of concentrated waste streams. For certain such applications lime has proved more effective and has been used in full-scale applications where lime addition can be integrated into the production process (for example, in the removal of organic color from Kraft pulp mill waste where lime precipitation can be integrated with the chemical recovery step in the pulping process). Lanthanide salts, which hydrolyze to a much lesser extent and can effect removals over a broader pH range than Al(III) and Fe(III) salts, have been investigated for application to wastewater treatment for phosphate removal (3).

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*In smaller applications, chemicals are often added directly to the feed pump inlet with the mixing taking effect in transit.

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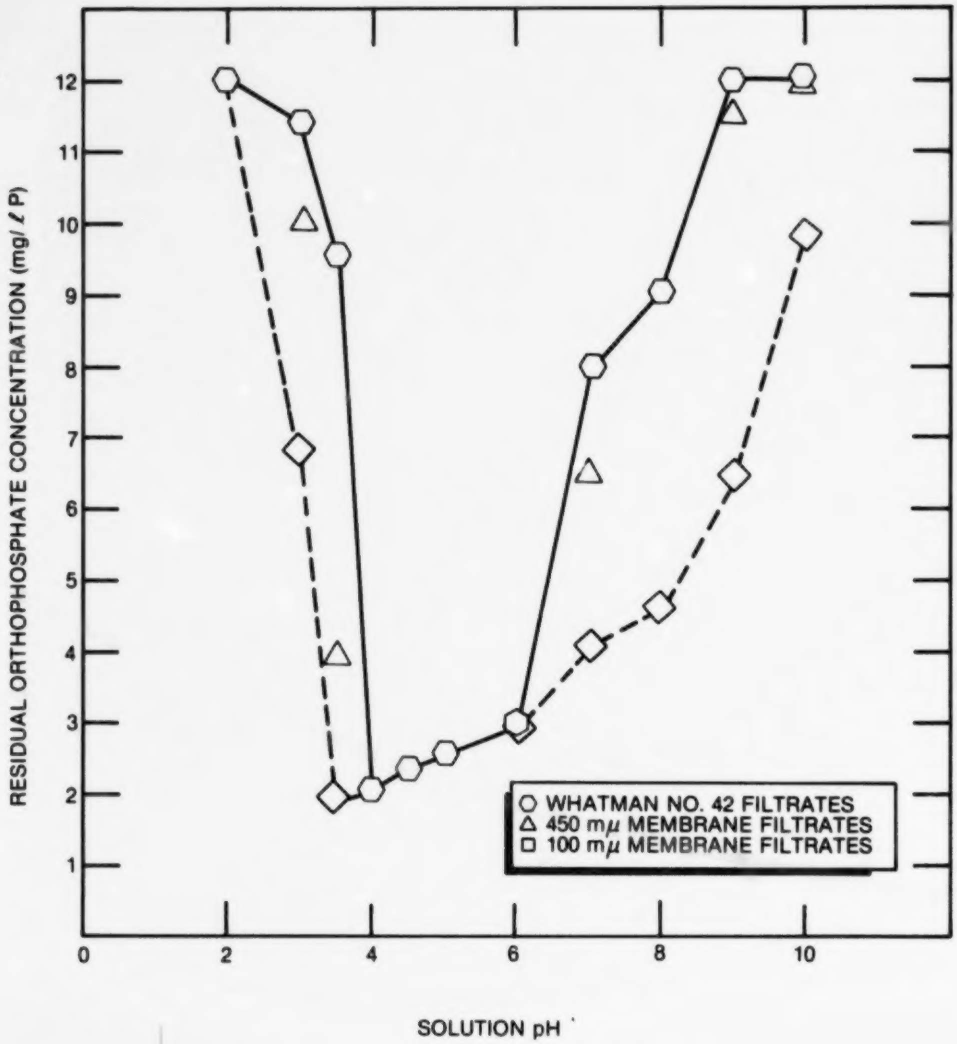

Figure 15. Residual orthophosphate in precipitation of orthophosphate with Fe(III) at a 1:1 cation-to-orthophosphate molar ratio (2) (Initial orthophosphate concentration, 12 mg/ℓP).

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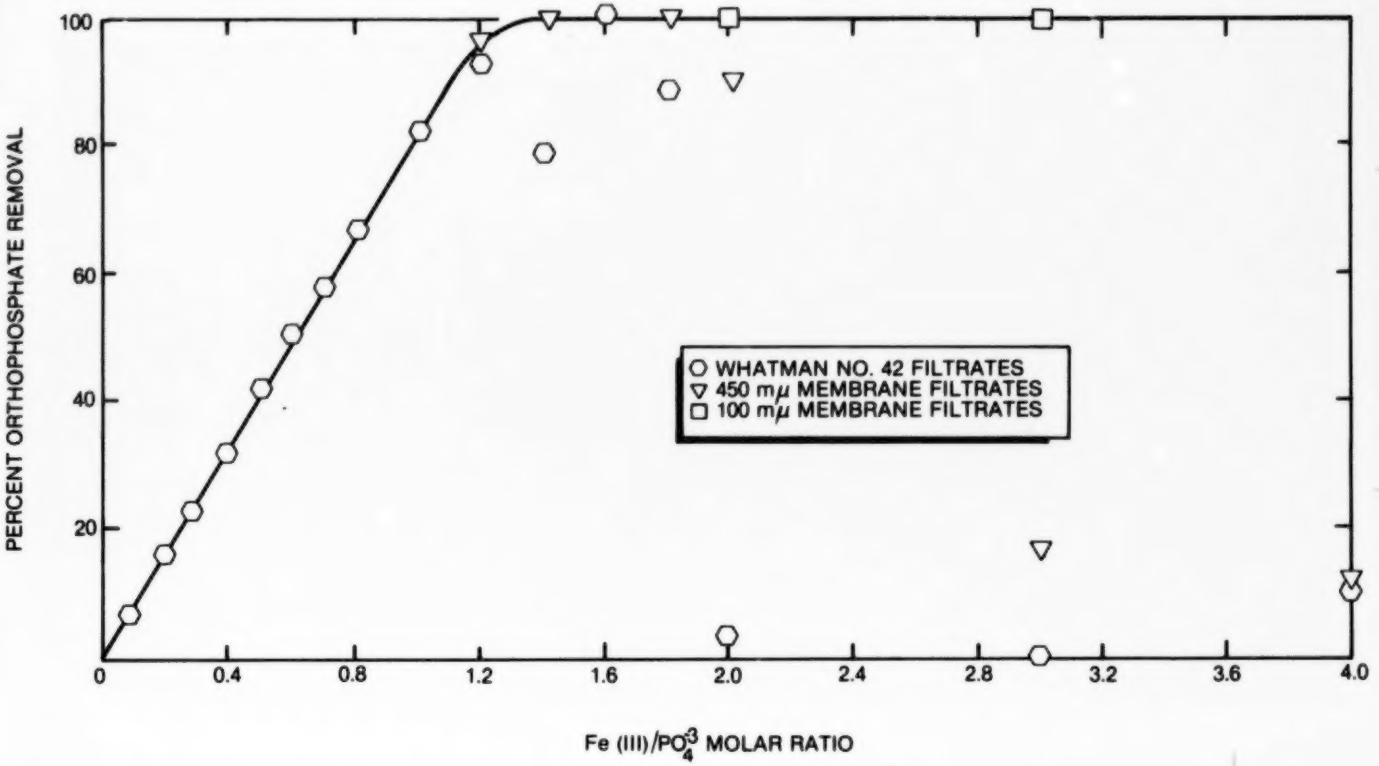

Figure 16. Orthophosphate removal in Fe(III)-orthophosphate reaction at pH 4.0 (initial orthophosphate concentration, 12 mg/ℓP) (2).

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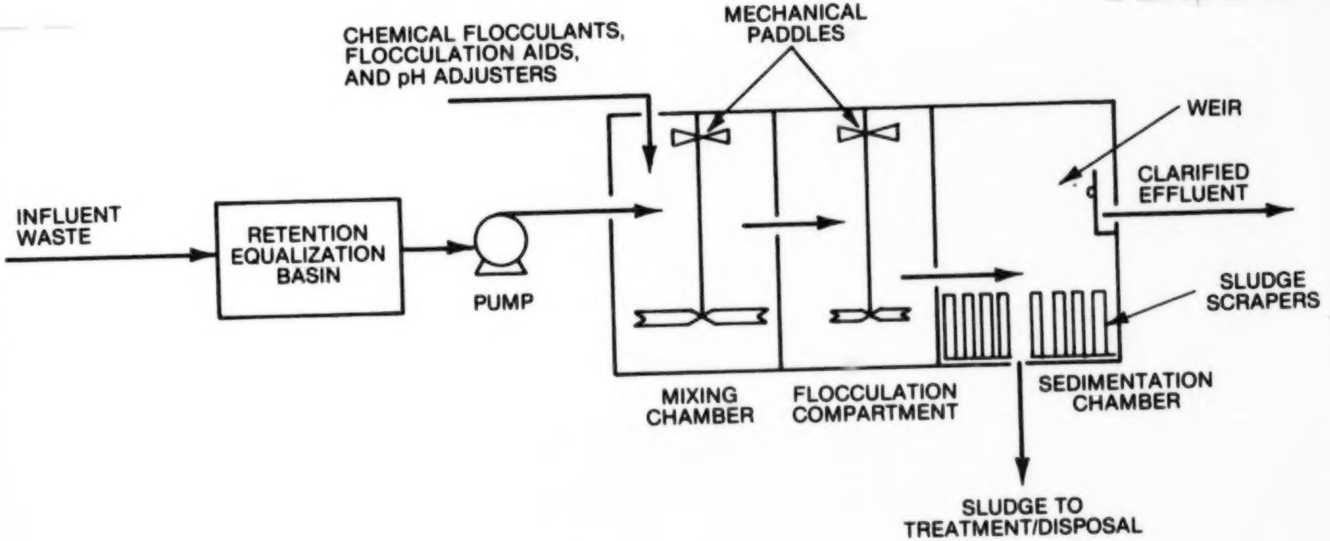
CHEMICAL FLOCCULANTS, FLOCCULATION AIDS, AND pH ADJUSTERS
MECHANICAL PADDLES
WEIR
CLARIFIED EFFLUENT
INFLUENT WASTE
RETENTION EQUALIZATION BASIN
PUMP
SLUDGE SCRAPERS
MIXING CHAMBER
FLOCCULATION COMPARTMENT
SEDIMENTATION CHAMBER
SLUDGE TO TREATMENT/DISPOSAL

Figure 17. Schematic of coagulation - flocculation system.

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PROCESS APPLICATIONS AND RELATED STUDIES

Commercial Scale Municipal/Industrial Applications

Chemical precipitation and coagulation is widely used in the treatment of municipal and industrial water supplies for the removal of particulates, hardness, and naturally occurring organic color ("humic" substances). Hydroxide and sulfide precipitation have been used in full-scale processing of industrial wastewaters for the removal of heavy metals (for example, hydroxide precipitation of dissolved copper and nickel from the effluent from copper sulfate production, and of lead, chromium, and zinc from effluent from chrome pigment production (4)).

Lime, ferric, aluminum, and ferrous salts have been used in combination with biological or physical wastewater treatment processes to precipitate phosphates, improve particulate/floc settling and filtering characteristics, and to increase treatment plant throughput rate under overloaded conditions. These applications generally involve dilute systems and the chemical dosages are relatively small (100-300 ppm range). Where high concentration organic wastewaters are encountered, aluminum and iron salts have proved ineffective because of the very high chemical dosage requirement and the production of a large quantity of a "bulky" sludge that cannot be economically processed and disposed of. "Massive" lime treatment has been employed in large-scale application for the treatment of highly colored bleach waste in Kraft pulp mills. In this application the entire lime requirement of the mill is added to the bleach waste to effect substantial color removal; the organic-laden lime is then returned to the chemical recovery section of the mill where, as a process chemical, lime is used to regenerate the pulping liquor.

Pilot and Laboratory Scale Studies

Numerous laboratory and pilot plant studies have been reported in the literature on chemical treatment of actual and simulated industrial wastewaters and landfill leachates with aluminum and iron salts and lime. The most relevant of these studies from the standpoint of possible application to chemical treatment of concentrated waste spills and spill-impacted waters are those pertaining to landfill leachates.

Laboratory studies of the chemical treatment of landfill leachate with alum, ferric chloride, and lime have been reported (5). Treatment of a leachate containing 9,100 mg/ℓ COD with an alum dosage of 1,000 mg/ℓ yielded a COD removal of only 5.1 percent and a "substantial" amount of sludge. Treatment of the same leachate with 1,000 mg/ℓ of ferric chloride and at an optimum pH of 7.0 resulted in a COD removal efficiency of only 16 percent. Treatment of a leachate containing 10,650 mg/ℓ COD with a lime dosage of 1,840 mg/ℓ yielded a COD removal of only 3.5 percent. Color removal with lime, however, was excellent.

Chian and DeWalle (6) have summarized the results reported in the literature on the effectiveness of various physical and chemical processes for the treatment of landfill leachate. Their data indicate reported COD removal efficiencies with iron, alum, and lime ranging from 0 percent to as high as 31 percent.

USE IN MOBILE UNITS FOR THE TREATMENT OF WASTE SPILLS

Precipitation/coagulation per se merely involves addition to and rapid mixing of the chemicals in the raw water. For continuous operation, metering devices and chemical pumps are used for continuous feeding of the chemicals in dry, slurry, or solution form. Chemical addition is followed by flocculation and settling and/or filtration. The equipment used for these subsequent operations and their suitability for use in mobile units are discussed later in connection with the EPA's Mobile Physical/Chemical Treatment System and in connection with biological oxidation.

The cost for chemical feed system for use in mobile units would be less than $3,000. Chemical costs would vary with the type of chemical used and the dosage required. The current costs for alum (17 percent Al_2O_3), ferric chloride, and lime are reportedly $161/mt, $110/mt, and $36/mt, respectively (7).

REFERENCES

1. Ghassemi, M. and H.L. Recht. Precipitation of Polyphosphate with Aluminum and Ferric Salts, paper presented at the 25th Purdue Industrial Waste Conference, Lafayette, Indiana, May 5-7, 1970.

2. Recht, H.L. and M. Ghassemi. Kinetics and Mechanism of Precipitation and Nature of the Precipitate Obtained in Phosphate Removal from Wastewater Using Aluminum (III) and Iron (III) Salts, Federal Water Quality Administration, Water Pollution Control Research Series 170/OEKI04/70, April 1970.

3. Recht, H.L., M. Ghassemi, and E.V. Kleber. Precipitation of Phosphates from Water and Wastewater Using Lanthanum Salts, Proceedings of the 5th International Water Pollution Research Conference, San Francisco, CA, July-August 1970.

4. Development Document for Interim Final Effluent Limitations Guidelines and Proposed New Source Performance Standards for the Significant Inorganic Products Segment of the Inorganic Chemicals Manufacturing Point Source Category, EPA Report EPA-440/1-75/037, 1975.

5. Ho, S., W.C. Boyle, and R.K. Ham. Chemical Treatment of Leachates from Sanitary Landfills, Journal of Water Pollution Control Federation, Vol. 46, No. 7, pp. 1776-1791, July 1974.

6. Chian, E. and F.B. Dewalle. Sanitary Landfill Leachates and Their Treatment, Journal of the Environmental Engineering Division, ASCE, 102, No. EE2, 411-431, April 1976.

7. Chemical Marketing Reporter, October 8, 1979.

SECTION 11

MISCELLANEOUS PROCESSES

Miscellaneous processes reviewed in this section include gravity separation, filtration, carbon adsorption, and thermal oxidation. These processes are commercially available and have been widely used for the treatment of municipal and industrial wastewaters and, except for the carbon adsorption, for concentration and disposal of sludges. With the exception of the thermal oxidation, these processes have also been used in mobile applications for waste treatability studies and for spill control. The review of the processes in this section is very brief and is primarily intended to make the study more complete.

Discussion of mobile unit applications of the various processes relies heavily on previous and current U.S. EPA experience in spills control, including the work on development and application of the Mobile Physical Chemical Treatment System and the Environmental Restoration Incinerator Complex (ERIC).

GRAVITY SEPARATION

Process Description

Gravity separation is a solids-liquid unit operation whereby particles denser than water are settled and collected as sludge, and particles lighter than water (for example, oil) are allowed to rise to the surface and are collected by skimming equipment. The efficiency of separation can be enhanced by addition of chemical coagulants and/or flotation agents.

Three of the most common types of gravity separators are the API separators, conventional settling tanks, and parallel plate/tube separators. In the API separator (Figure 18) the wastewater enters the basin and passes under the oil retention baffle, then over the diffusion baffle (to minimize turbulence). As the wastewater travels the length of the channel, the oil globules move toward the surface and the heavy particles settle downward. Flight scrappers push the oil that has reached the surface towards one end and into the slotted pipe for removal. At the same time the flight scrappers push sludge deposits on the bottom of the basin to sludge hoppers. Clarified water passes under the oil retention baffle and leaves the unit.

Conventional settling tanks are circular or rectangular in design. In the circular design the influent enters at a central location and effluent is collected around the tank periphery. The sludge is collected in a central hopper.

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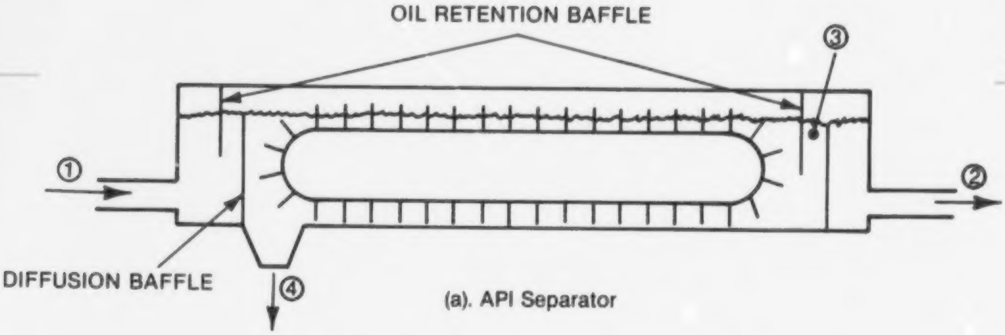
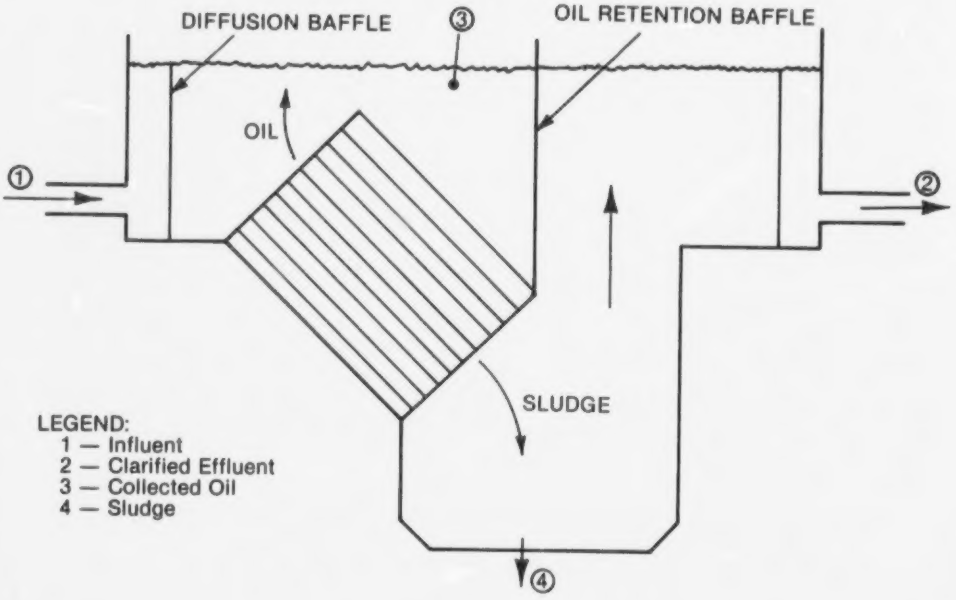

OIL RETENTION BAFFLE
③
①
②
DIFFUSION BAFFLE
④

(a). API Separator


DIFFUSION BAFFLE
③
OIL RETENTION BAFFLE
OIL
①
②
SLUDGE
LEGEND:
1 — Influent
2 — Clarified Effluent
3 — Collected Oil
4 — Sludge
④

(b). Parallel Plate Separator

Figure 18. Gravity separators.

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In parallel plate (or tube) separators (Figure 18), the wastewater enters the separator and flows over a weir and through the parallel plates (or tubes). The plates can either be corrogated or flat. The oil particles coalesce on the underside of the plates and rise up to the surface where they are removed. Solids collect on the bottom of the plates and slide downward toward the sludge hopper for removal.

Gravity separators are widely used for the treatment of municipal and industrial wastewaters and they often constitute the first module in wastewater treatment trains. Because of differences in the characteristics of various wastewaters (for example, nature and concentration of suspended solids, temperature of feed stream, presence or absence of emulsions), design and operation of separators must be "tailored" to the specific wastewaters to be treated. Depending on the wastewater characteristics and the unit loading, a suspended solids removal efficiency of as high as 70-80 percent can be achieved by gravity separation. Some general features of gravity separators from the standpoint of possible use in mobile units are listed in Table 23.

TABLE 23. GENERAL FEATURES OF GRAVITY SEPARATORS FOR USE IN MOBILE UNITS

Advantages	Disadvantages
Equipment very simple and easy to operate	Incomplete removal of suspended solids and no removal if dissolved solids
Units suitable for trailer mounting commercially available or can be readily fabricated	Settled solids require removal and disposal
Low energy consumption	
Can provide effective pretreatment for other processes	

Mobile Unit Applications

Although trailer-mountable gravity separation tanks are commercially available*, for logistic reasons, less "sophisticated" light-weight portable units are considered more suitable for use in connection with other spill treatment systems for field application. The EPA's Mobile Physical Treatment System uses large rubber, collapsable, portable tanks that are set up next to the trailer for pretreatment of wastewater by flocculation/sedimentation (1). The unit consists of two concentric tanks: a 11,350 ℓ (3,000 gal) reaction/flocculation center tank and a 56,775 ℓ (15,000 gal) sedimentation periphery tank. At a design flow rate of 12.6 ℓ/sec (200 gpm) the unit provides for a reaction/flocculation time of 15 minutes and a sedimentation time of 60 minutes. The raw waste is introduced at the bottom of the flocculation tank. Flocculation is achieved by hydraulic mixing via the use of two ejectors placed opposite to each other. The flocculated wastewater flows out of the center reaction tank into the 45,500 ℓ (12,000 gal) annular space of the sedimentation tank through a series of submerged orifices located around the periphery of the reaction tank. Both these tanks are cylindrical open top tanks and are supported by staves anchored into the ground. The open top tanks also permit easy accessibility for manual removal of sludge and floating materials.

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*For example, AFL Industries (Chicago, IL) markets a 10 to 500 gpm "Vertical Tube Coalescing Separator" (VTC) for the removal of oil and settleable solids from wastewaters (AFL Industries Bulletin No. 2-13.B.1 and supplementary information provided by Mr. Don Summer, Los Angeles Representative of AFL Industries). The unit is constructed of fiberglass with PVC fittings and has overall dimensions of 4.8 m length, 2.3 m width, and 2.1 m height (14 ft x 7.7 ft x 6.7 ft). The unit weighs 2,050 kg (4,500 lb) when empty and 6,840 kg (15,050 lb) when loaded.

A 11.9 ℓ/sec (50 gpm) sludge pump and special suction fittings are provided for removal of settled and floating contaminants and a 11,350 ℓ (3,000 gal) rubber stave tank is provided for storage. The sludge can subsequently be pumped out of the stave tank by the sludge pump into a tank truck or other container for further treatment and/or final disposal.

FILTRATION

Process Description

Filtration is a unit operation employed to remove suspended solids from water and wastewaters*. A flow diagram of a typical filtration system for the removal of suspended solids from liquids is shown in Figure 19. Wastewaters are slowly percolated through a bed of filter media (for example, sand, charcoal, diatomaceous earth, anthracite, etc.). Suspended solids are collected on the surface and in the interstices of the filter. The accumulation of the solids on and in the filter media results in an increase in pressure drop (or head loss) across the filter bed. When the pressure drop becomes "excessive" (usually 1.5 to 2.4 m of water column), the filter is backflushed to remove the suspended solids from the surface and interstices of the filter. Backwash water contains a very high concentration of suspended solids and is usually treated by sedimentation (for example, in primary sedimentation unit that precedes filtration).

Depending on the design and operating conditions, a water very low in turbidity can be obtained by conventional sand filtration. Chemical coagulant may be added to the filter influent to increase particle removal efficiency and/or extend the filter "run". Table 24 lists some general features of

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*Filtration is also used for solid concentration (e.g., in dewatering of sludges); this type of filtration is not considered in this discussion.

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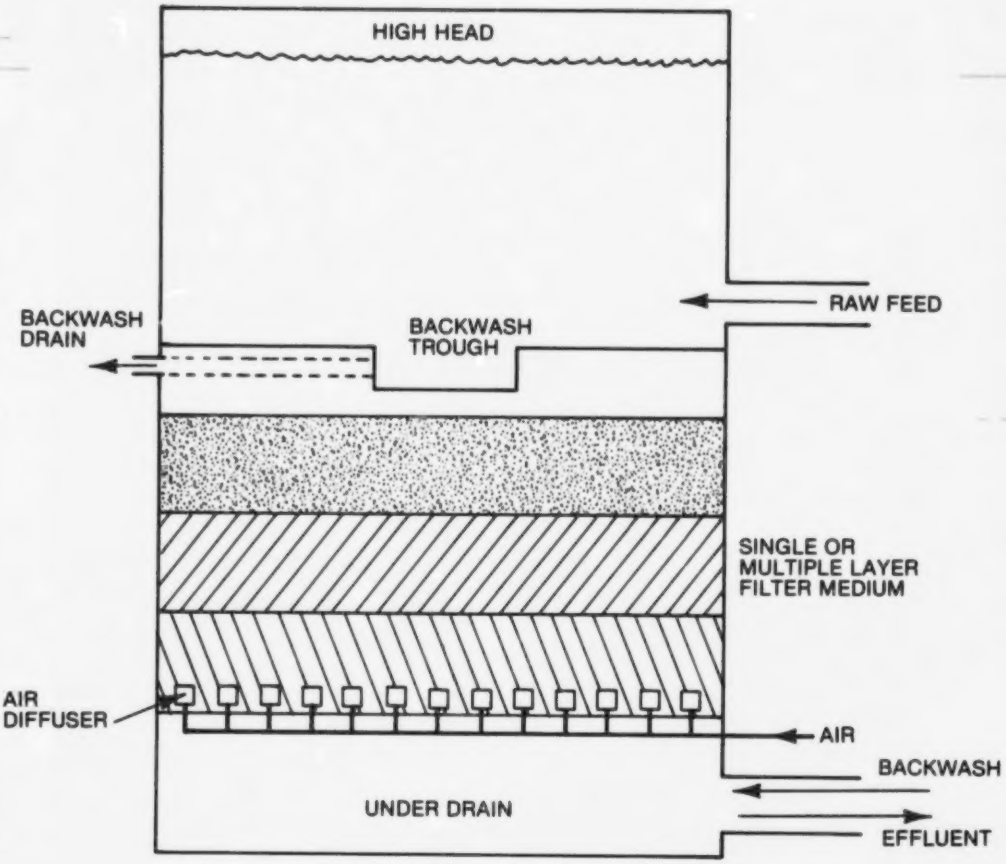
HIGH HEAD
RAW FEED
BACKWASH DRAIN
BACKWASH TROUGH
SINGLE OR MULTIPLE LAYER FILTER MEDIUM
AIR DIFFUSER
AIR
BACKWASH
UNDER DRAIN
EFFLUENT

Figure 19. Typical filtration bed.

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conventional filtration from the standpoint of use in mobile units for wastewater treatment.

TABLE 24. GENERAL FEATURES OF FILTRATION FOR APPLICATION TO WASTEWATER TREATMENT IN MOBILE UNITS

Advantages	Disadvantages
Equipment reliable, simple, and commercially available	Ineffective in removal of dissolved substances
Ability to handle wide fluctuations in influent suspended solids concentrations	Produces backwash wastewater containing high solids concentration
Ease of operation and control	Frequent backwashing of filter required when treating influent high in suspended solids
Can provide effective pretreatment for other processes	
No secondary air pollution problem	
Considerable experience exists in mobile unit application	

Mobile Unit Applications

The EPA's Mobile Physical/Chemical Treatment System, which has been in operation for more than six years, incorporates three "dual" media (sand-anthracite) filters in its treatment train. The three filter units are connected in parallel and may be taken off line individually for backwashing. The filters consist of 61 cm (24 in) anthracite over 45 cm (18 in) fine sand and are designed for a maximum hydraulic loading of 4.8 ℓ/sec/m^2 (7.0 gpm/ft^2). Additional features of the filters are described in Table 25.

The supernatant from the sedimentation tank is drawn off by the filter pump through a submerged orifice header ring at the outside tank wall. A pneumatic level sensor in the sedimentation rank controls filter pump flow to match raw flow. After the addition of a filtration conditioner, the settled effluent is pumped through the three dual media filters in parallel for removal of residual suspended solids. Two in-line turbidimeters monitor the turbidity of the total filter influent and effluent from each tank. A differential pressure gauge indicates the degree of filter clogging. The filters are backwashed with air and clean system effluent stored in a 11,350 ℓ (3,000 gal) pillow tank. The backwash waste is pumped to a 11,350 ℓ (3,000 gal) stave tank. From here it can be pumped out by the sludge pump either into a tank truck for disposal or it may be reintroduced into the raw feed line and recycled through the system. The air-backwash system is arranged so that two filters may be left on line while one is taken off line for backflushing.

TABLE 25. FEATURE OF A DUAL-MEDIA FILTER UNIT USED IN THE EPA'S MOBILE PHYSICAL/CHEMICAL TREATMENT SYSTEM (1)

Filter diameter	1.17 m (3.5 ft)
Filter area	0.893 m^3 (9.62 ft^2)
Design filtration rate	2.11 ℓ/sec (33.5 gpm)
Maximum filtration rate	4.22 ℓ/sec (67 gpm)
Design backwash rate	6.3 ℓ/sec (100 gpm)
Maximum allowable differential pressure	1.06 kg/m^2 (15 psi)
Maximum tank pressure	4.93 kg cm/cm^2 (70 psi)
Depth of sand	45 cm (18 in)
Effective size	0.5 mm
Uniformity coefficient	1.5
Quantity of sand	860 kg (1,900 lbs)
Depth of coal	61 cm (24 in)
Effective size	0.85 - 9.85
Uniformity coefficient	1.7
Quantity of coal	0.425 m^3 (15 ft^3) 0.39 ton

CARBON ADSORPTION

Process Description

Carbon adsorption is a unit operation for the removal of soluble organics from wastewaters. Removal of the soluble organics is affected by contacting the wastewater with activated carbon. Two methods of contact are commonly used: passing wastewater through a column or bed of granular activated carbon and adding powdered activated carbon directly to a treatment system. Spent granular activated carbon containing adsorbed organics is usually regenerated by thermal treatment. Powdered activated carbon is in most cases not recovered and is disposed of with other wastewater treatment sludges.

Granular activated carbon systems commonly employ two or more beds and provide for continuous treatment with periodic removal of one of the adsorbers from service for backwashing and removal of spent carbon*. Backwashing serves to remove particulate buildup on the column surface that increases bed pressure drop, thereby increasing energy consumption. A schematic diagram of a two-vessel carbon adsorption system is shown in Figure 20.

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*Fixed beds may be arranged in series or parallel with either upflow or downflow design. "Pulsed" columns with countercurrent flow of carbon and wastewater have also been used.

Regeneration of the spent carbon is performed by thermal regeneration in a furnace. The regeneration process produces offgases that must be treated for particulate, odor, carbon monoxide, residual organics, and hydrocarbon removal. Wastewaters resulting from bed backwashing, reactivated carbon quenching, and air emission controls are usually returned to upstream treatment systems.

Use of powdered activated carbon for wastewater treatment has several drawbacks, including unavailability of commercial regeneration systems, difficulty in handling large dosage requirement, and production of sludge requiring disposal.

Removal of an organic compound by activated carbon is affected by the characteristics of the specific carbon used (adsorbent), the specific substances to be removed (adsorbate), and the solution properties (pH, temperature, nature, and characteristics of other dissolved solids in the wastewater). In general, activated carbon preferentially adsorbs high molecular weight and less polar organic compounds. Table 26 shows the relative adsorbability of several representative compounds differing in structure and molecular weight. In actual wastewater applications, a wide range of substances would be encountered and the actual carbon performance would have to be determined by laboratory and pilot testing. Critical design criteria are contact time and organic loading. Contact time defines the adsorber size and number of units required. The amount of organic material removed per weight of carbon determines the carbon usage rate and the regeneration requirements.

Activated carbon systems for wastewater treatment are employed in industries such as coke production, oil refining, petrochemical production, and pesticide manufacture. Carbon systems are also used for trace organics, taste and odor removal from potable water supplies, sugar decolorization, and purification of fats, oils, foods, beverages, and pharmaceuticals. In commercial refinery applications, from 59 percent to 83 percent COD removal has been obtained with granular carbon systems used without prior biological treatment. Studies of an activated carbon system for treatment of a coke plant effluent after clarification and filtration reported 80 percent COD removal, 91 percent TOC removal, and 99 percent phenol removal. Even though these removal efficiencies are very high, the effluent from activated carbon adsorption can contain substantial concentration of organics (for example, in the case of concentrated waste spills). Some general features of activated carbon adsorption as a treatment process for the removal of organics from wastewaters are listed in Table 27.

It is estimated that there are approximately 100 large-scale carbon adsorption systems in use for industrial/municipal waste treatment (5). A number of carbon manufacturers own and operate trailer-mounted carbon adsorption units that are used to assess treatability of industrial wastes and/or to develop criteria for the design of large-scale carbon adsorption units for industrial application.

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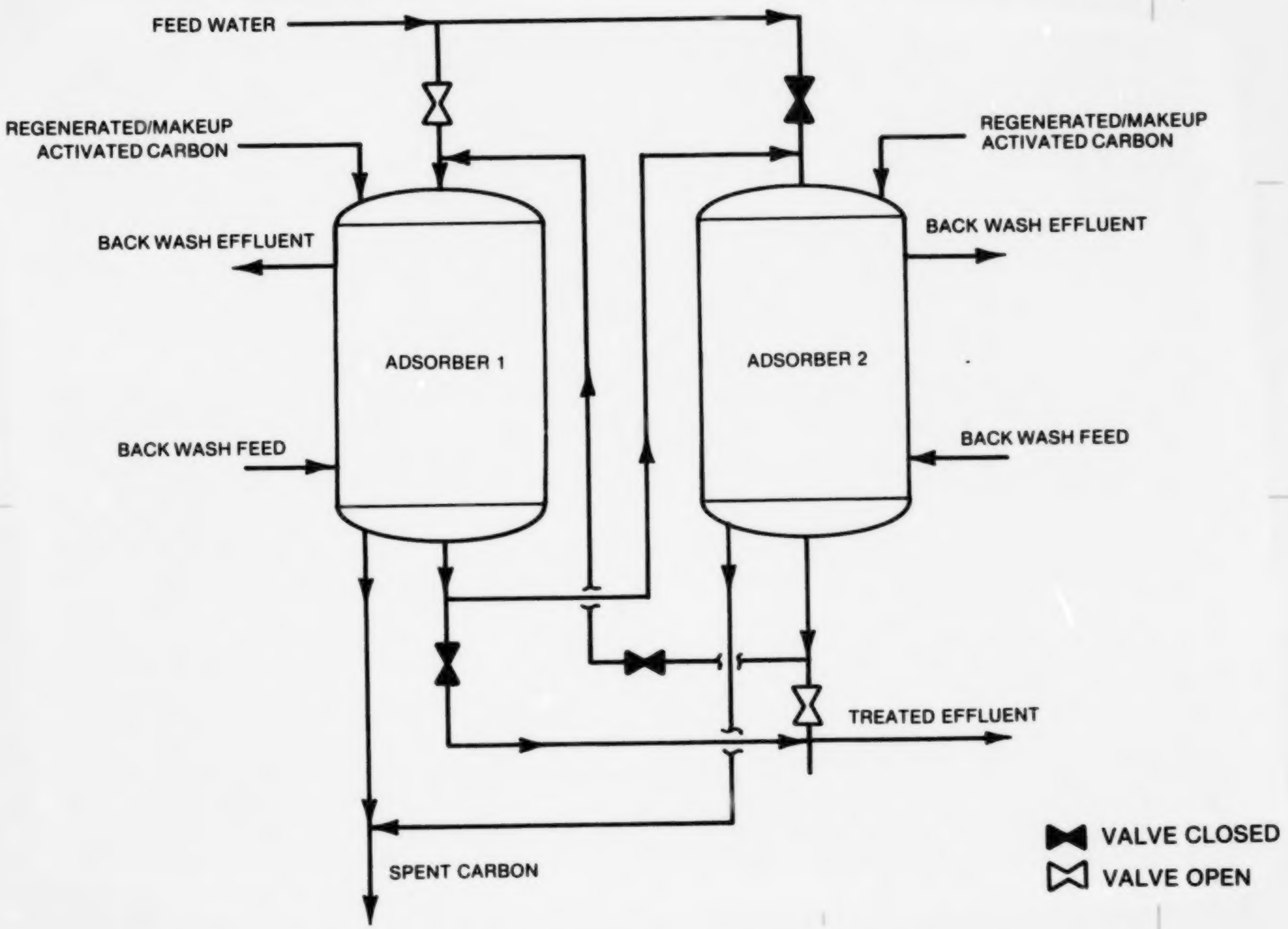
FEED WATER
REGENERATED/MAKEUP ACTIVATED CARBON
REGENERATED/MAKEUP ACTIVATED CARBON
BACK WASH EFFLUENT
BACK WASH EFFLUENT
ADSORBER 1
ADSORBER 2
BACK WASH FEED
BACK WASH FEED
TREATED EFFLUENT
SPENT CARBON
VALVE CLOSED
VALVE OPEN

Figure 20. Two-vessel granular carbon adsorption system (2).

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TABLE 26. AMENABILITY OF TYPICAL ORGANIC COMPOUNDS TO ACTIVATED CARBON ADSORPTION* (3)

Compound	Adsorbability† (grams compound/grams carbon)
Ethanol	0.02
2-ethyl butanol	0.170
Acetaldehyde	0.022
Benzaldehyde	0.188
Di-n-butylamine	0.174
Monoethanolamine	0.150
2-methyl 5-ethyl pyridine	0.179
Benzene	0.080
Hydroquinone	0.167
Ethyl acetate	0.100
Butyl acetate	0.193
Isopropyl ether	0.162
Ethylene glycol	0.0136
Tetraethylene glycol	0.116
Acetone	0.054
Acetophenone	0.194
Formic acid	0.047
Valeric acid	0.159
Benzoic acid	0.183

*Westvaco Nuchar WV-G (12 x 40 mesh, coal based) carbon.

†5 g carbon added to 1 liter of solution containing 100 mg/ℓ of compound.

TABLE 27. SOME FEATURES OF ACTIVATED CARBON ADSORPTION PROCESS FOR REMOVAL OF ORGANICS FROM WASTEWATERS

Advantages	Disadvantages
High efficiency of organics removal	Generally limited to wastes with less than 1 percent organic content
Applicable to a wide range of organics, including toxic organics not amenable to biological treatment	High capital and operating cost
Low sensitivity to variations in feed concentrations	Pretreatment of waste to reduce suspended solids concentration generally necessary
Relatively small space requirements	Does not remove most inorganic substances
Commercially available	In mobile unit application, on-site regeneration may not be practical and spent carbon may require ultimate disposal
Considerable operating experience available, including use of trailer-mounted units	

Mobile Unit Applications

The U.S. EPA's Mobile Physical/Chemical Treatment System (1), which has been in operation for more than six years, uses three activated carbon columns that handle the effluent from the dual-media filters. The filtered effluent flows through three pressure carbon columns that may be used in parallel or in series. Altogether, they contain 19.6 m^3 (700 ft^3) of carbon. This volume represents a dry carbon weight of 8,172 kg (18,000 lb) of carbon, which is the maximum possible weight that can be accommodated on the trailer because of the overall weight constraints on the mobile system. The carbon columns are designed for a hydraulic loading rate of 3.4 ℓ/sec/m^2 (5 gpm/ft^2). Three 2.1 m (7 ft) diameter carbon columns with carbon bed depth of 1.8 m (6 ft) are provided on the mobile treatment system. The selected carbon volume of 19.6 cu m (700 cu ft) on the trailer provides a maximum contact time of 27 minutes for the three columns at a flow rate of 12.6 ℓ/sec (200 gpm). This carbon contact time has been found to be suitable for many of the hazardous materials evaluated. However, when high contact times are required, these may be provided by reducing proportionately the hydraulic flow rates through the carbon columns.

The carbon tanks, which occupy the back one-half of the trailer, are completely plumbed so that only valve adjustments are necessary to control the various modes of operation. The trailer is designed so that it may be transported with the carbon columns full of the wet, drained carbon. However, whether done on the site or back at the homebase, the carbon will need to be recharged either because of exhaustion, to prevent undesirable effects of mixing contaminants, or because storage with contaminants in the carbon could be hazardous. Spent carbon may be removed using the backwash pump and processed clean water stored in one of the rubber tanks for this purpose. The clear effluent water is pumped through the underdrain system of the carbon column to fluidize the bed and cause the slurry to drain out of the tank drain fitting.

When the adsorptive capacity of the carbon for the processed hazardous materials is depleted, new carbon may be installed into the tanks in the field by a slurry pumping system. Depletion time, or breakthrough, occurs simultaneously for parallel operation and sequentially for series operation. Thus all of the carbon must be replaced at once for parallel operation as opposed to one tank at a time for series operation. The tank plumbing permits a rotation of the flow sequence through the tanks for series operation. Thus, the leading tank eventually becomes the second tank in line and finally assumes the third position until breakthrough and carbon replacement, whereon it again assumes the first position. The slurry pumping system for carbon replacement utilizes a dry carbon hopper feeding an eductor through which clean effluent from the effluent storage tank is pumped to form a slurry. The slurry is pumped into the carbon column where it is dewatered by the carbon column underdrains. The water is then returned to the effluent storage tank completing the closed loop slurry pumping system. A manual sampling valve in the carbon column inlet line and in each tank effluent line permits analysis of process water to measure removal effectiveness and to sense carbon column breakthrough.

Table 28 summarizes some operating results for the treatment of a number of spill-impacted waters by the EPA's Mobile Physical/Chemical Treatment System.

INCINERATION

Process Description

Incineration is the thermal destruction of wastes in a controlled environment. It has been used for the destruction of toxic organic wastes and disposal of municipal and industrial sludges.

Several types of incinerators that are in commercial use include the following: fluidized bed, rotary kiln, multiple hearth, and liquid injection. Some key features of these incinerators are summarized in Table 29. Incinerators for the destruction of hazardous wastes should provide a sufficiently high temperature and residence time in the combustion chamber to assure near complete destruction of the organics.

Figure 21 depicts the basic components and input/output streams associated with the rotary kiln incinerator. The basic components consist of the following:

- a waste storage and waste feeding mechanism
- fuel-fired burner and oxidation chamber (may include afterburner, not shown)
- flue gas purification system (usually a wet scrubber with liquid collection tank)

TABLE 28. TOXIC COMPOUNDS REMOVED FROM WATER USING EPA'S MOBILE PHYSICAL/CHEMICAL TREATMENT SYSTEM (6)

Compound	Location of incident	Quantity treated (ℓ)	Contact time (min)	Influent conc. (mg/ℓ)	Effluent conc. (mg/ℓ)	Removal (%)
DNBP	Clarksburg, N.J.	7,600,000	26	8	<0.002	99.98
PCB	Seattle, Wash.	2,270,000	30-40	400	<0.075	99.98+
		45,000,000	8.5	1	<0.075	92.5+
Toxaphene	The Plains, Va.	950,000	26	36	1	97.22
Chlordane	Strongstown, Pa.	380,000	17	13	0.35	97.3
		11,400	240	1,430	0.43	99.99
Heptachlor	Strongstown, Pa.	380,000	17	6.1	0.06	99.02
		11,400	240	80	0.1	99.87
Aldrin	Strongstown, Pa.	380,000	17	8.5	0.19	97.76
		11,400	240	60.5	0.15	99.75
Dieldrin	Strongstown, Pa.	380,000	17	11	<0.01	99.99+
		11,400	240	60.5	<0.01	99.99+
Kepone	Hopewell, Va.	850,000	45.5	4,000	<1	99.98
Pentachlorophenol	Haverford, Pa.	820,000	26	10,000	<1	99.99
Methylene chloride	Oswego, N.Y.	950,000	8.5	190	51	73.15
Carbon tetrachloride	Oswego, N.Y.	950,000	8.5	1.1	<0.1	90.91+
Benzene	Oswego, N.Y.	950,000	8.5	1	0.1	90
Toluene	Oswego, N.Y.	950,000	8.5	120	0.3	99.75
Xylenes	Oswego, N.Y.	950,000	8.5	140	<0.1	99.92+
Trichloroethane	Oswego, N.Y.	950,000	8.5	12	<0.1	99.17+
Trichloroethylene	Oswego, N.Y.	950,000	8.5	21	0.3	98.57
Phenol	Oswego, N.Y.	950,000	8.5	140	<0.1	99.92+
Cresol	Oswego, N.Y.	950,000	8.5	230	8.1	96.47
Dimethylphenol	Oswego, N.Y.	950,000	8.5	1,220	5.4	99.56
Trimethylphenol	Oswego, N.Y.	950,000	8.5	130	10	92.3
Butylphenol	Oswego, N.Y.	950,000	8.5	300	15	95
Dioctyladipate	Oswego, N.Y.	950,000	8.5	360	320	11
Dimethylaniline	Oswego, N.Y.	950,000	8.5	380	23	93.95
PCB	Dittmer, Mo.	180,000	60	19	<0.1	99.47+

TABLE 29. KEY FEATURES OF MAJOR TYPES OF INCINERATORS (7)

Type	Process principle	Application	Combustion temp.	Residence time
Rotary kiln	Slowly rotating cylinder mounted at slight incline to horizontal. Tumbling action improves efficiency of combustion.	Most organic wastes; well suited for solids and sludges; liquids and gases.	810-1,640°C (1,500-3,000°F)	Several seconds to several hours
Multiple hearth	Solid feed slowly moves through vertically stacked hearths; gases and liquids fed through side ports and nozzles.	Most organic wastes, largely in sewage sludge; well suited for solids and sludges; also handles liquids and gases.	760-980°C (1,400-1,800°F)	Up to several hours
Liquid injection	Vertical or horizontal vessels; wastes atomized through nozzles to increase rate of vaporization.	Limited to pumpable liquids and slurries (750 SSU or less for proper atomization).	650-1,650°C (1,200-3,000°F)	0.1 to 1 second
Fluidized bed	Wastes are injected into a hot agitated bed of inert granular particles; heat is transferred between the bed material and the waste during combustion.	Most organic wastes; ideal for liquids, also handles solids and gases.	750-870°C (1,400-1,600°F)	Seconds for gases and liquids; longer for solids

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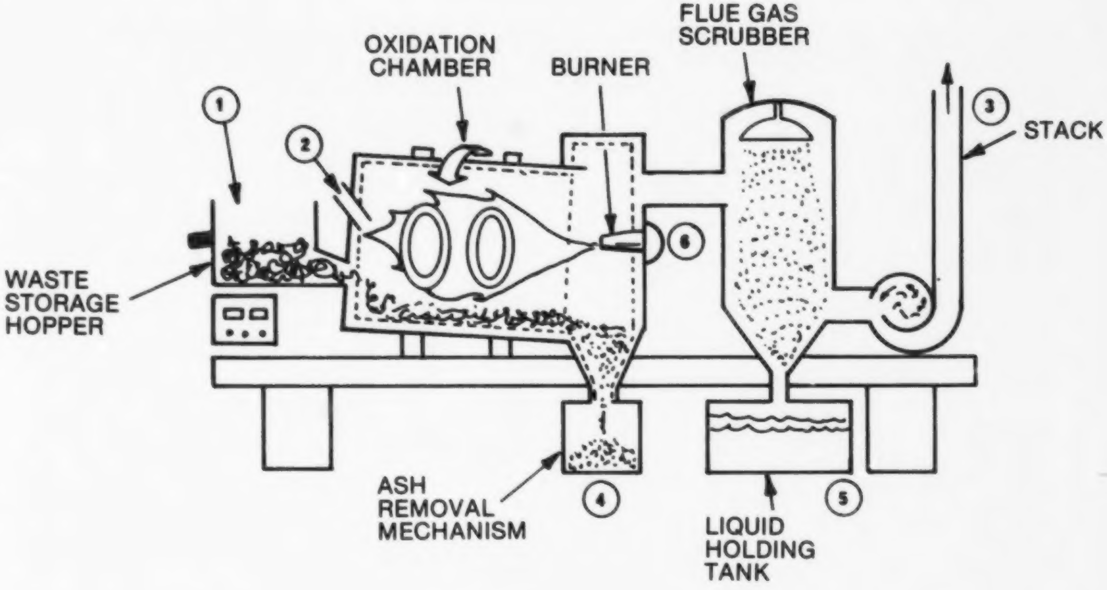
OXIDATION CHAMBER
BURNER
FLUE GAS SCRUBBER
①
②
③
STACK
WASTE STORAGE HOPPER
⑥
ASH REMOVAL MECHANISM
④
⑤
LIQUID HOLDING TANK

LEGEND:
1. INFLUENT WASTE
2. COMBUSTION AIR
3. FLUE GAS
4. RESIDUALS
5. SCRUBBER WATER
6. FUEL

Figure 21. Rotary kiln incineration unit.

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- ash removal mechanism
- flue gas stack or vent

All incineration processes require some auxiliary fuel to initiate combustion and bring the oxidation chamber up to temperature. Depending on the heat content of the waste, auxiliary fuel may or may not be required during incineration. Some incineration systems (especially those used for hazardous waste incineration) may require an afterburner to insure complete destruction of organics.

The effluent streams from the incineration process are ash and the scrubber water. The ash is generally inorganic inerts and has a small volume. Scrubber waters have high inorganic solids content and are usually treated before disposal. Some advantages and disadvantages of incineration as a process for the disposal of hazardous organic wastes are summarized in Table 30.

TABLE 30. SOME ADVANTAGES AND DISADVANTAGES OF INCINERATION SYSTEMS FOR THE DESTRUCTION OF TOXIC ORGANIC WASTES

Advantages	Disadvantages
Effective for destruction of solid, liquid and gaseous toxic organic wastes	High degree of process control required to insure efficient operation, especially when highly halogenated organic wastes are to be destroyed
Reduces waste to a small volume of inerts (ash) which can be disposed of safely	Use of afterburners and scrubbing systems required to minimize air pollution
Incineration technology well developed and considerable experience exists in connection with hazardous waste destruction	Ash and scrubber water require disposal
	Auxiliary fuel required for wastes low in Btu content

Mobile Unit Applications

M.B. Associates (San Ramon, CA) is currently under an EPA contract to design, construct, and demonstrate a mobile incineration system for destruction of residuals from hazardous material spill clean-up operations. The system, referred to as the Environmental Restoration Incinerator Complex (ERIC), will be mounted and transported on three heavy duty truck trailers. As shown in Figure 22, Trailer No. 1 houses the control room, ram feeder, loading bin, shredder, and rotary kiln; Trailer No. 2 houses the afterburner and the quench unit, whereas the scrubber, blowers and diesel generators are loaded on Trailer No. 3. Each trailer unit will be 13.7 m (45 ft) and when pulled by a tractor will meet most interstate requirements for both width and

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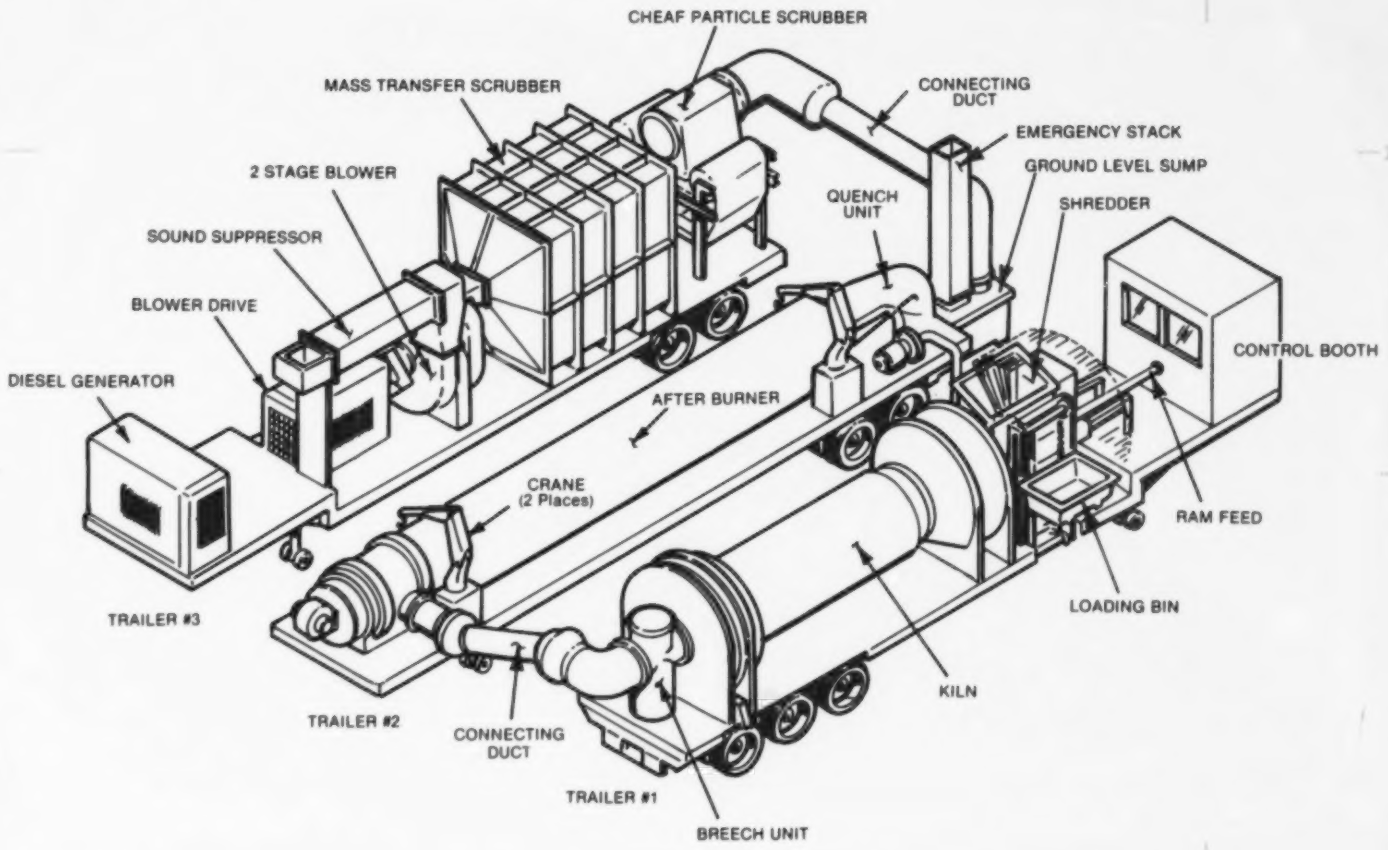
CHEAF PARTICLE SCRUBBER
MASS TRANSFER SCRUBBER
CONNECTING DUCT
EMERGENCY STACK
2 STAGE BLOWER
GROUND LEVEL SUMP
QUENCH UNIT
SHREDDER
SOUND SUPPRESSOR
BLOWER DRIVE
CONTROL BOOTH
DIESEL GENERATOR
AFTER BURNER
CRANE (2 Places)
RAM FEED
LOADING BIN
TRAILER #3
KILN
TRAILER #2
CONNECTING DUCT
TRAILER #1
BREECH UNIT

Figure 22. Mobile environmental restoration incinerator complex.

length. Some key design concepts incorporated in the Mobile ERIC system include the following:

- All components must be suitable and compatible with both over-the-road and off-the-road shock and vibration loads.
- The system must be capable of processing solids, liquids, and sludges with or without Btu content.
- Kiln temperatures of 1,800°F to insure volatilization of HM's with one hour dwell for solids in order to assure clean ash residuals.
- Afterburner minimum temperatures of 2,012°F per Federal Regulations of PCB's.
- Afterburner two second dwells to insure thermal decomposition of pesticides and poly-chlorinated biphenyls per Federal Regulations.
- Excess O_2 above 3 percent per Federal Regulations.
- Particle scrubbing sufficient to effectively meet a 10 percent permanent plume opacity when decomposing organic phosphates that will generate P_2O_5.
- An absorber scrubber to effectively meet SO_2 and HCl emission constraints for incinerators at various locations.

Since the Mobile ERIC has not yet been field tested, no operating data are available on its application to spill clean-up wastes.

REFERENCES

1. Gupta, M.K. Development of a Mobile Treatment System for Handling Hazardous Material Spills, EPA Report No. 600/2-76-109, July 1976.

2. U.S. EPA, Process Design Manual for Carbon Adsorption, EPA 625/1-71-002a, October 1973.

3. Giusti, D.M., et al. Activated Carbon Adsorption of Petrochemicals, Journal of Water Pollution Control Federation, Vol. 46, No. 5, May 1974.

4. Van Stone, G.R. Treatment of Coke Plant Waste Effluent, Iron and Steel Engineer, April 1972, pp 63-66.

5. Arthur D. Little. Physical, Chemical, and Biological Treatment Techniques for Industrial Wastes, NTIS PB-275-287, November 1976.

6. La Fornora, J. Cleanup After Spills of Toxic Substances, Journal of Water Pollution Control Federation, April 1978.

7. Shen, T., M. Chen, and J. Lauber. Incineration of Toxic Chemical Wastes, Pollution Engineering, October 1978, pp 45-50.